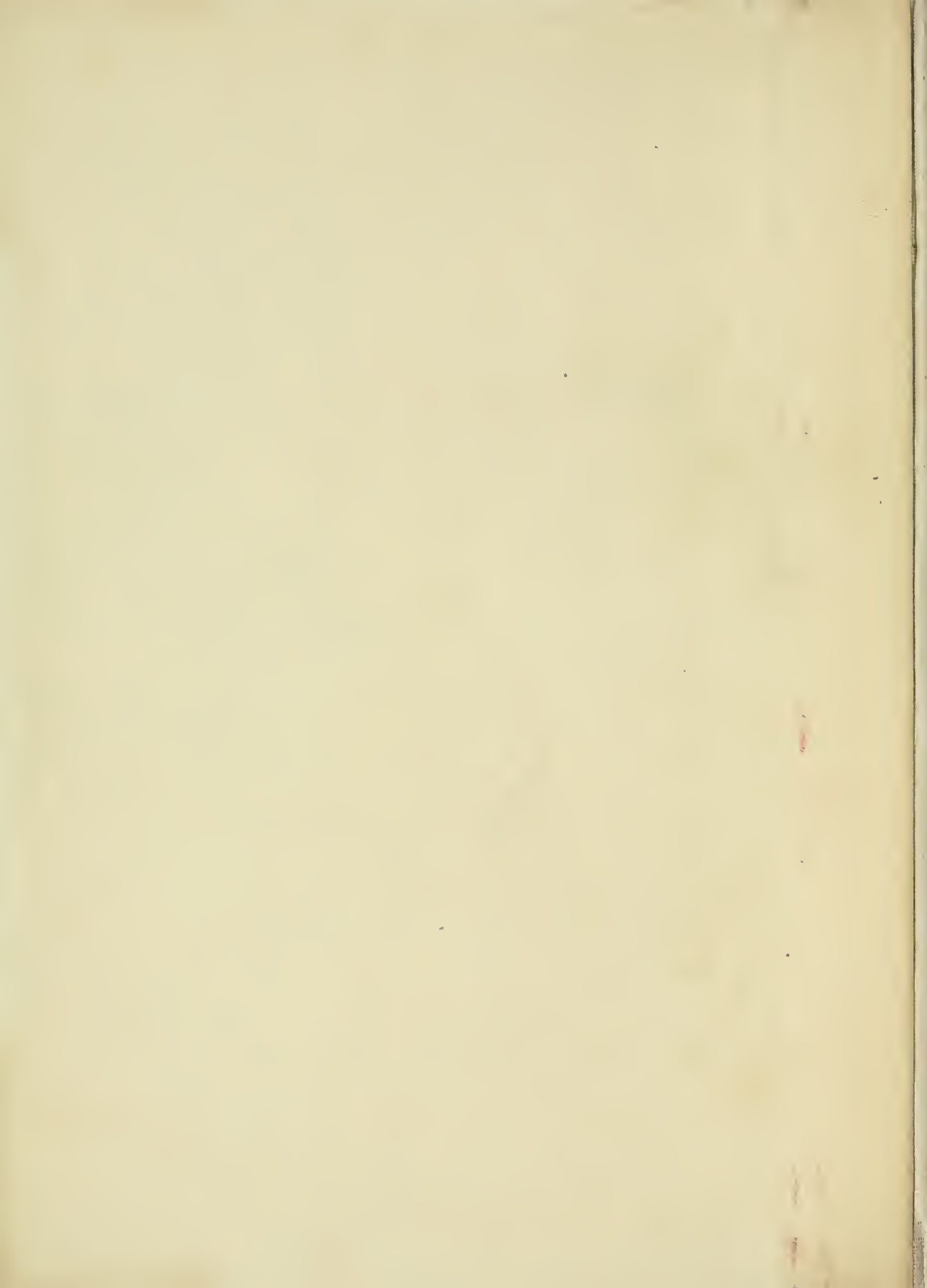


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THE CHEMICAL NEWS, JULY 31, 1914.

THE
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IN ALL ITS APPLICATIONS TO

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SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

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THE CHEMICAL NEWS.

VOLUME CIX.

EDITED BY SIR WILLIAM CROOKES, O.M., D.Sc., Pres.R.S., &c.

No. 2823.—JANUARY 2, 1914.

REVIEW AND INTERPRETATION OF RECENT EXPERIMENTS WHICH EXTEND AND ELUCIDATE THE DOMAIN OF THE PASSIVITY OF METALS.*

By Dr. D. REICHENSTEIN, Zurich.

1. Historical.

FARADAY (Letter to Brayley, July 8, 1836, *Lond. and Edinb. Phil. Mag.*, 1836, ix., 122) ascribes the discovery of the passivity to Keir (*Phil. Trans.*, 1790, pp. 374 and 379), who observed in 1790 that iron was not attacked in strong nitric acid, but assumed a "changed" state.

The problem was, however, investigated only in the thirties of the last century by Faraday and by Schönbein; the latter introduced the term "passivity." The difference of opinion between the two originators of the problem is of high historical interest. Faraday's views as to the nature of passivity were interpreted by Schönbein (*Pogg. Ann.*, xxxvii., 390; xxxviii., 444; xxxix., 342) to the effect as if Faraday saw the cause of the passive behaviour of a metal in the formation of a well-developed oxide on the metallic surface, and Faraday is still frequently being called the originator of the oxide theory of passivity. In my opinion Faraday may with equal right be regarded as the originator both of the oxide theory and of the most modern theories of gas charges and metal-oxygen alloys; and in this sense I regard the theory which I am going to present merely as a logical consequence of the views of Faraday.

In support of this statement I quote the beginning of a letter which Faraday addressed to R. Taylor (*Phil. Mag.*, 1837, x., 175) on January 21, 1837:—

"Dear Sir,—I am much obliged to you for a sight of Mr. Schoenbein's paper, the experiments and observations in which are excellent. The cause of the phenomena he has so well distinguished is indeed exceedingly difficult to be distinguished at present, and I was in hopes that the doubt on my mind when I ventured the view referred to would be evident from my words. My strong impression is," &c. (*Phil. Mag.*, 1836, ix., 61). "Moreover, Mr. Schoenbein and also M. Alb. Mousson, in an attempt which he has made to explain the cause (*Bibliothèque Universelle de Genève*, 1836, p. 165), have not given my view clearly. I have said that my impression is that the surface of the metal is oxidised, or else that the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation,

meaning by that, not an actual oxidation, but a relation. . . ."

Faraday further alludes to the researches of Nobili on the colours of thin plates, and he expresses the view that the latter went much further still in the opinion that skins of oxygen and acid may lastingly adhere to the surfaces of platinum, iron, and steel without entering into chemical combination with the metal.

The above quoted letter by Faraday to Taylor further contains, near its end, the following words:—"And my opinion of the cause of the phenomena as due to a relation of the superficial particles of the iron to oxygen. . . ."

From these views of Faraday has arisen the oxide theory of passivity which has been advocated up to the most recent days (e.g., by F. Haber and F. Goldschmidt, *Zeit. Elektrochem.*, 1906, xii., 49).

The theory which I am going to develop is further connected with the views of M. Le Blanc (*Zeit. Elektrochem.*, 1900, vi., 476), who first expressed the idea that it is velocity phenomena which condition passivity. This assumption has successfully been developed and specialised by Fredenhagen (*Zeit. Elektrochem.*, xi., 857, and *loc. cit.*), who makes the occurrence of passivity dependent upon "a coherent, uniform gas charge"; finally Muthmann and Fraunberger (*Sitzber. Bayer. Akad. Wissensch. München: Math.-Phys. Kl.*, 1904, 236) have recognised that this gas charge has the character of an alloy.

The question now, which I put to myself, and which is not discussed by any of the actual theories, is how the transition is taking place from the active state of a metal into the passive state. This question is to receive an answer which can quantitatively be tested by calculations.

Before we pass to the discussion of this question, however, we have to acquaint ourselves with a series of experiments of the very latest dates, some of which have extended the domain of passive phenomena, while others are able to introduce us into the labyrinth of passivity.

2. Chemical Polarisation of Reversible Active Metallic Electrodes.

Before the year 1910 all the metals were distinguished as active and passive, and if there was a tendency to look for the cause of passivity in slowly progressing chemical reactions, i.e., in a slow rate of ion-formation, people held on the other side that with active metals anodically treated the formation of ions took place with infinite velocity, and that any polarisation observed with active metals had to be designated a concentration polarisation or a diffusion polarisation; that is to say, a polarisation which arose owing to the differences in the concentration of the electrolyte caused by the current flow, whilst

* A Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, November 12, 1913. (Translated from the German.)

diffusion tended to balance this difference in concentration.

I should like to emphasise in this place already that these definitions of chemical or of concentration polarisation are inappropriate, and that they fail in complicated cases. For the occurrence of concentration differences is not characteristic for the diffusion polarisation. With one and the same electrode different polarisations are observed, always as results of different concentrations of the substances in question. The point is rather, which process is opposing the differences in concentrations to which the electric current gives rise, *i.e.*, whether this compensation is of a chemical nature or a diffusion phenomenon. Hence it would, in my opinion, be appropriate to introduce a definition like the following:—If in any observed polarisation the substitution of a real process by an imaginary chemical process, proceeding at infinite velocity, would make the polarisation vanish, we should have to deal with a *chemical polarisation*; if a *diffusion* proceeding at infinite rate should have the same effect, we should have to deal with a *diffusion polarisation*.

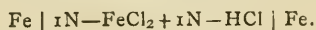
Now Le Blanc described in 1910 some experiments which have revolutionised our conception of active and passive metals ("Die elektromotorischen Kräfte der Polarisation"). Two proofs can be adduced that there is only a quantitative, not a qualitative, difference between active and passive metals, and that there is, in active metals, a possibility not only of a diffusion polarisation, but also of a chemical polarisation.

These are the proofs:—

In 1904 Thatcher observed that when quite small quantities of so called poisons are added to an electrode, at which an electrolytic oxidation is taking place, the anode potential rises considerably, which indicates that slowly progressing chemical reactions are at play. Le Blanc and his assistants now demonstrated that an addition of poisons to the active electrode $\text{Cu} | \text{CuSO}_4$ called forth the same effect. Thus 1 cc. of a faintly acid solution of brucine sulphate (of 1 per cent.), added to 100 cc. of a solution of $1\text{N}-\text{CuSO}_4 + 1\text{N}-\text{H}_2\text{SO}_4$, raises the cathodic polarisation from 29 to 148, and the anodic from 14 to 40 millivolts. Strychnine raised the cathode polarisation by 115, the anode polarisation by 18 millivolts, &c.

When we further compare the polarisations of two electrodes under conditions, as equal as possible, of temperature, current density, concentration of the ions, &c., and when we consider that the diffusion rates must, under those equal conditions, be of the same order of magnitude, we are entitled to conclude that large differences in the polarisation values of the two electrodes can only arise owing to the chemical polarisation of that electrode which possesses the higher polarisation value.

Thus the system $\text{Hg} | 0.1\text{N}-\text{HgNO}_3 + 1\text{N}-\text{HNO}_3 | \text{Hg}$ gave, at a current density of 0.09 amp./cm.², a polarisation of about 6 millivolts, whilst under the same conditions the system $\text{Cu} | 1\text{N}-\text{CuSO}_4 + 1\text{N}-\text{H}_2\text{SO}_4 | \text{Cu}$ gave, with electrodes of Cu quenched in methyl alcohol, 30 millivolts, and with Cu electrodes polished with emery 110 millivolts. Still higher polarisations, of the order of 500 millivolts, were obtained with the system—



The third proof for the existence of the chemical polarisation of active electrodes was given by Haber and Zawadzki (*Zeit. Physik. Chem.*, 1912, lxxviii., 241) in 1912, in a paper on the polarisation of solid electrolytes. They found that "solid silver salts show, with a silver anode, a polarisation which increases considerably with falling temperature, and which, in the case of silver sulphate, becomes so pronounced at the temperature of solid carbon dioxide, that the silver anode behaves like an anode of platinum or graphite."

A further proof for the existence of the chemical polarisation of active electrodes is afforded by the fact that

additions of free sulphuric acid and of its salts to the $\text{Cu} | \text{CuSO}_4$ electrode much increase the cathodic polarisation (R. Goebel, "Dissertation," Dresden, 1912, researches carried out under F. Foerster; also D. Reichstein, *Zeit. Elektrochem.*, 1913, xix., 520, and D. Reichstein and A. Zieren, *Ibid.*, 530). These two accounts do not yet contain the results of all the experiments made. In order to keep the effect of an addition of a neutral salt quantitatively reproducible, the electrolyte should possess a certain minimum of H^+ ions; for below a certain H^+ ion concentration the cathodic current intensity-potential curve of the $\text{Cu} | \text{CuSO}_4$ electrode takes a qualitatively quite different course from the curve found above this minimum. That indicates that it is purely chemical processes which are responsible for the current intensity-potential curve. Since now all the neutral salts as well as the sulphuric acid itself have the same effect, the increased polarisation is evidently due to the fact that the addition diminishes the concentration of the Cu ions in the electrolyte. What kind of a polarisation is this then—a chemical or a diffusion polarisation?

The first-mentioned case must not be confounded with another, in which the electrolyte contains the same small concentration of Cu^{++} ions, but in which the neutral salt and the noteworthy concentration of undissociated CuSO_4 are missing in the electrolyte.

In contrast to this simple case the more complicated case may be discussed as follows:—Imagine an ideal case, in which the Cu electrode has a considerable concentration of the Cu ions (a), the required minimum of H^+ ions, and a very small (practically none) concentration of undissociated CuSO_4 molecules. At a certain current density at which the cathodic polarisation is still zero, a large amount of some alkali salt is added to the electrolyte, in order to reduce the concentration of the Cu ions to $\frac{a}{10}$, *e.g.*, and to set up a certain definite polarisation at the same time. Let us further assume the existence of an electrode which, in the presence of the $\frac{a}{10}$ concentra-

tion of its ions (without, however, possessing the 0.9*a* concentration of the undissociated salt) will mark, *ceteris paribus*, the same polarisation as the Cu electrode referred to. The comparison between this hypothetical electrode and the really existing Cu electrode would suggest:—On the one hand (case 1) the polarisation of the Cu electrode would be caused by a slow (*i.e.*, secondary) transition of the ions into the metallic state; it is assumed that while the current is flowing the concentration of the ions is, by vigorous stirring, kept the same at the electrode surface as in the middle of the electrolyte. On the other hand (case 2) the polarisation of the Cu electrode might be caused by the difference in the concentration near the electrode and in the middle of the electrolyte. The comparison between the Cu electrode and the hypothetical electrode now teaches—

The latter case (2) is only possible when the rate at which the spent Cu ions are replenished by the reaction $\text{CuSO}_4 \rightarrow \text{Cu}^{++} + \text{SO}_4^{--}$ is infinitely small compared with the rate of diffusion of the Cu ions from the middle of the electrolyte to the surface of the electrode.

The following criteria enable us to distinguish between case 1 and case 2:—

If we can find an electrode such that the concentration of its ions be only $a/10$, that it contain no undissociated salt, and that it do not display any polarisation, *ceteris paribus*, then that Cu electrode would belong to case 1.

If we further succeed in constructing an electrode such that, with an ion concentration of $a/10$, it show *ceteris paribus* the same polarisation as our Cu electrode, but practically do not, in an electrolyte of the composition 0.1*a* concentration of its ions + 0.9*a* concentration of the undiss-

sociated salt, possess any polarisation, that would be our case 2. It should be added that case 1 represents a pure example of chemical polarisation, whilst case 2 may be regarded as chemical polarisation and as diffusion polarisation as well. For, according to the definition formulated above, in case 2 the polarisation would vanish: by substitution of the real rate of dissociation of the CuSO_4 by an infinitely rapid rate of dissociation, and also by substitution of the real rate of diffusion of the Cu ions by an infinitely rapid rate of diffusion.

These complicated polarisation phenomena may probably be more easily investigated in practice than it would appear from this deduction; for I consider that the compensation process of case 2 will, in the predominating number of examples, practically be conditioned only by the dissociation of the undissociated salt. We shall thus either have case 1, or have case 2, in which the dissociation of an undissociated salt will represent the compensation process. The further investigation of the Cu electrode, undertaken for the purpose of deciding the question whether the chemical polarisation owes its existence to the dissociation process indicated, or perhaps to the reduction of the Cu ions (slow because of the small concentration of the latter), has suggested a solution of the problem in favour of case 1 (*loc. cit.*). This consideration is of principal importance for electrodes whose electrolytes consist of complex salts, e.g., $\text{Ag} | \text{Ag}(\text{CN})_2\text{K} |$ electrode.

Interesting examples of chemical polarisation, again not due to slow diffusion of the electrolyte, can be observed when the Cu electrode is rubbed with a little mercury. These cases will be explained lower down.

In looking for an example of an electrolysis which would supply a simple analogy to the described cases of chemical polarisation, that is to say, which would render clear how chemical polarisation can occur with an active electrode, without the metallic electrode losing its capacity of primarily (see Note) furnishing ions—in looking for such an analogy (which has been found) a whole series of phenomena was recognised as exemplifying negative depolarisation.

(NOTE.—By a primary electrochemical reaction we understand a reaction with which the passage of the current through the boundary electrode-electrolyte is connected, e.g., the charging of a metallic atom with an electron, or the discharge of an ion. Since this reaction proceeds in synchronism with the electric current, it is more rapid than all chemical reactions—practically of infinite velocity. If the anodic formation of Cu ions progressed primarily, undisturbed, that would not cause any chemical polarisation. The fact that chemical polarisation does occur indicates that another primary reaction is proceeding, and that the Cu^+ ion formation is secondary).

3. Negative Depolarisation.

(Reichenstein, *Zeit. Elektrochem.*, 1913, xix, 520).

What is a depolariser? Imagine a circuit, consisting of a source of electric current having a constant e.m.f. independent of the load, and of a polarisation cell, e.g., of two platinum electrodes in clay cells charged with diluted sulphuric acid, these pots themselves immersed in a common beaker also filled with H_2SO_4 . We close the circuit after the current intensity has reached its stationary value, and we add to the electrolyte about the cathode a solution of CuSO_4 . Then a partly new process will set in at the cathode, and the current intensity will rise. Any material capable of producing these two effects simultaneously is usually called a depolariser. The action of the depolariser appears especially clear to us when it is soluble in the solvent which constitutes the electrolyte, and particularly when it does not chemically react with the electrolyte to which it is added, and does not disturb the state of this electrolyte.

Are there now such materials which, when added to the electrolyte, will not chemically react with it, and will diminish the current intensity instead of increasing it?

In other words, are there any negative depolarisers? The reply to this question must decidedly be in the affirmative. Let the cathode of the described circuit consist, not of Pt, but of a $\text{Pd}-\text{H}_2\text{SO}_4$ electrode. When the electrode has, from the beginning, a small H_2 concentration, the electrolysis at not too high current densities will proceed in such a way that the whole hydrogen will be occluded by the electrode, and the polarisation will be very small. We have probably to deal with a very rapid chemical compensation process constituted perhaps by the reaction between the Pd atoms and the primarily formed H atoms.

If we now add, during the electrolysis under suitable conditions, a zinc salt to the electrolyte, the polarisation will increase, the current intensity in the circuit diminish, and a new process will set in: zinc is deposited on the cathode (*Zeit. Elektrochem.*, 1910, xvi.).

The surprising feature in this phenomenon is that, of all the possible processes, it is generally the more rapid which takes place. Which means in the case of the zinc addition that that process which occurs more easily will be impeded, namely, the deposition of hydrogen from the electrolyte by the zinc which would be deposited in minimal quantities (not to be determined by weighing), even at open circuit owing to local action. The zinc hence strengthens the chemical inertia of the reaction between the Pd and H atoms, and acts as a depolariser in a negative sense. I should like to point out in this place already that, if we desire to explain the chemical polarisation of a metallic electrode—let it scarcely be recognisable, or, on the other hand, sufficiently marked to lead to a generation of oxygen at the anode (=passivity)—without denying to the metallic atoms the capability of forming primary ions, then the discharge of OH^- ions, which with anodic treatment is simultaneous with the process of charging the atoms, may be regarded as the first step of a negatively depolarising reaction. The analogy is patent; we need only build up the mechanism of the chemical polarisation in a correct way.

The behaviour of real alloys on the anode may further be recognised as an example of negative depolarisation. A. Bürger and I (*loc. cit.*) have anodically investigated the alloys Cu—Ag, Cu—Hg, Cd—Hg, and Cd—Ag.

The noble metals, in amounts as small as possible, are alloyed with the surface of the baser metals. All the alloys examined have qualitatively the same property: they raise the polarisation whilst the equilibrium potential remains equal to that of the unalloyed chemically pure electrode. Thus the polarisation of a Cu electrode which has been rubbed with a little mercury rises *ceteris paribus* from 33 to 161 millivolts. The anodic current density-potential curve of the alloys shows under certain conditions a point of inflection. The alloy is decomposed when the electrolysis is prolonged, and the nobler constituent aggregates or drops down from the electrode.

Of special interest for all these alloys is a strange relation between the velocity of formation of the alloy and the degree of polarisation attainable with the resulting alloy. The Cu electrode may simply be amalgamated by holding it horizontally, the surface free from paraffin facing upward, and pouring some mercury on it, finally adding a few drops of concentrated nitric acid. When the electrode is quickly rinsed with distilled water, a bright mercury surface is left; the nitric acid in this operation plays the part of the soldering liquid in the soldering process.

An electrode prepared in this way, however, hardly marks any greater polarisation than the pure unamalgamated Cu electrode.

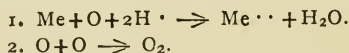
In order to prepare an electrode which will show the effect described of the amalgamated Cu electrode, every trace of HNO_3 must be avoided, and the greatest care be observed to deal with pure metals. The mercury is rubbed in the dry into the chemically pure copper surface; this is a tedious operation, and the slower the alloy formation the higher will afterwards be the polarisation realised under anodic treatment.

To the phenomena of negative polarisation might perhaps be joined another class of phenomena. In the cathodic polarisation of mixtures of nickel sulphate and zinc sulphate, of the sulphates of nickel and iron, and of zinc and iron, the polarisation rises frequently up to the value of the baser metal, and this latter metal is likewise deposited (A. F. Walter von Escher, "Kathodische Vorgänge bei der Elektrolyse gemischter Lösungen von Zink- und Eisensulfat," Dissertation, Dresden, 1912; a full literature list will be found there; compare also F. Foerster, "General Electrochemical Behaviour of Metals," *Zsit. Elektrochem.*, 1908, xiv., 153). These processes are not pure examples of negative depolarisation, however, because in the absence of the less noble metal the more noble one is deposited quantitatively, i.e., with a current efficiency of 100 per cent; at the same time hydrogen is generated. These cases are worthy of attention when one of the two metals at least in the salt mixture which is being electrolysed belongs to the cathodically passive metals.

To these experiments, which, as we shall see, introduce us into the ante-room of the passivity phenomena, others may be added, which initiate us directly into the secrets of passivity.

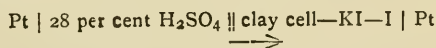
4. Direct Experiments on the Passivation of Metals.

Surprise has often been expressed at the fact that a metal turning passive does not, at higher current density, show at least that anodic solubility which belongs to it at small current density. Let a passive metal be dissolved anodically at a low current density a to the extent of 50 per cent, and let it liberate oxygen, so that its dissolution takes place at $\frac{a}{2}$ amp./cm.² of metallic surface. When we increase the current intensity tenfold, the dissolution will not proceed at the rate of 5a amp./cm.²; it does not even take place at the former rate $\frac{a}{2}$ amp., but at a much smaller rate. How is this to be interpreted chemico-kinetically? Let us assume that a passive metal Me generates primarily oxygen. Two reactions are possible:—



The commencement of reaction (2) is designated "passivity." The example teaches us that passivity is not a result of two competing reactions, for both of which the velocity would increase with increasing oxygen concentration, but: *the passivity is caused by two reactions such that the velocity of the one reaction decreases with increasing O concentration, whilst the velocity of the second reaction regularly increases with increasing O concentration.*

In 1911 I set myself the task to investigate how the rate of increase of the anodic polarisation potential accompanying the flow of continuous current through a Pt—H₂SO₄ electrode differs in the two cases when the Pt electrode is free from oxygen and when it has previously been charged with O₂ (Reichstein, *Zeit. Elektrochem.*, 1911, xvii., 89; 1913, xix., 672). I made the following observations:—A current impulse is imparted to the combination—



in the direction of the arrow. Its anodical amplitude is 0.1 amp./cm.² of the Pt electrode, its duration 0.026 second. After the expiration of this period follows a spontaneous diminution in the electrode charge lasting 0.028 second. The rest of the anodic charge is then destroyed by short-circuiting the cell for 0.025 second. These three processes succeed one another. (The arrangement comprises a

rotating commutator which closes the primary circuit, interrupts it, and closes the short-circuit; the latter could be opened and closed at will during an experiment with the aid of a cut-out). In this way it was possible to obtain, on a photographic plate, oscillographs of the time-potential curves at open and at closed short-circuit.

At open short-circuit this time-potential curve rises steadily up to an asymptotic potential value, which is independent of the time. At closed short-circuit the curve marks a point of inflection corresponding to the moment 0.004 second after closing the circuit. This point is well marked on the oscillogram, and the experiment is easily to be reproduced. I have been able to show this with the aid of the oscillographs at different times to several scientists.

This point of inflection can only be interpreted as indicating that we have to deal with a chemical reaction, the velocity of which first increases and then decreases, as the current quantity (i.e., together with the oxygen concentration) is increasing. During a period which is smaller than 0.004 second the time-potential curve has the distinct tendency of approaching the time ordinate and a stationary value at low potentials. Every approach to a stationary condition now is connected with an increase in the velocity of the compensation process, i.e., of that process in the absence of which the stationary conditions could not be reached. Now we observe a point of inflection within 0.004 second after closing the circuit, when the potential rises; the velocity of the compensation process is beginning to fail.

Thus the curve velocity-oxygen concentration possesses a maximum.

The compensation process consists of the formation of platinum oxides (see below).

During a period which is smaller than 0.004 second, therefore, a Pt | H₂SO₄ electrode behaves, at a current density of 0.1 amp./cm.², like an inattackerable electrode. The amount of Pt oxide which is formed per sq. cm., when the continuous current is not interrupted, is hence of the order of magnitude 0.004 · 0.1/96540 = 4 · 10⁻⁹ grm.-equivalent.

When afterwards the electrode is polarised for some time with the short-circuit closed, the electrode becomes covered with a yellowish layer which consists of Pt oxides. This does not occur when the short-circuit is open. We remember that platinum is dissolved with a high current yield in KCN solutions by alternating currents, but not by continuous currents. A combination, continuous currents superposed on alternating currents, is utilised in the gold industry.

A lucky accident has led us to the direct experimental recognition of the described maximum of the curve, in which the velocity is plotted as a function of the oxygen concentration.

In Russia a large amount of gold is gained by dissolving the ores in aqueous KCN solution in the presence of air as oxidising agent. This process being very slow, there has been no lack of attempts of trying other oxidising agents.

In this connection Andrejew (*Journ. Russ. Phys. Chem. Soc.*, 1907, xxxix., 1637; *Nachricht. Polyt. Inst., Petersburg*, 1908, ix., 447; *Zeit. Elektrochem.*, 1913, xix., 667) and later Michailenko and Meschterjakow (*Journ. Russ. Phys. Chem. Soc.*, 1912, xlv., 567)—on the instigation of Kistiakowsky—determined the rate of solution of gold in KCN in the presence of oxidising agents. They all found that this dissolution takes place in such a manner that the rate first increases and then decreases with the concentration of the oxidising agent. The velocity-concentration curve displays a well-marked maximum.

We may now pass to the exposition of the theories which aim at bringing all the cases of chemical polarisation under one point of view.

(To be continued).

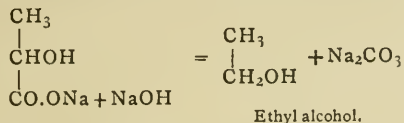
NOTE ON THE DECOMPOSITION OF HYDROXY ACIDS WITH SODA-LIME.

By LEONARD CARPENTER.

If we consider the reaction—

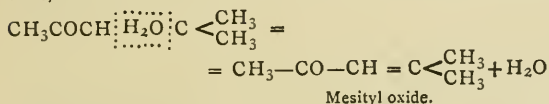


where R is an alkyl or aromatic radicle, such as methyl, ethyl, or phenyl, it might be imagined that, by heating the salts of hydroxy acids, alcohols might be obtained. For example, taking lactic acid, if its sodium salt be heated with soda-lime, the following reaction might take place:—

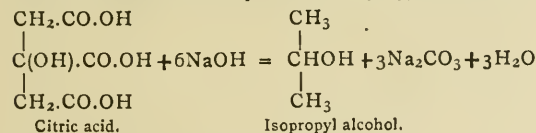


In order to test this, sodium lactate, intimately mixed with soda-lime, was destructively distilled in an iron tube under reduced pressure at a temperature just below redness. A distillate was obtained consisting of two layers, an upper one consisting of a brown oily liquid, having an odour of peppermint, and a lower aqueous one. By saturating the aqueous portion with solid anhydrous potassium carbonate a liquid was separated which turned out to be acetone. The brown oily portion of the distillate appeared to consist mostly of mesityl oxide.

It is evident, therefore, that ethyl alcohol, if formed, is at once oxidised. This is not surprising when it is remembered that alkalis can act as oxidising agents at high temperatures. One might imagine that the ethyl alcohol is first oxidised to acetic acid, which then loses water and carbon dioxide, giving acetone. This, by condensation of two molecules losing water, would give mesityl oxide, thus,—



Soda-lime acts as a powerful dehydrating agent. A similar experiment with citric acid gave the same products. In this case the theoretical product is isopropyl alcohol,—



This by oxidation gives acetone, which then undergoes condensation, giving mesityl oxide.

It is thus evident that in these pyrogenic reactions the theoretical first products are only formed, when they are highly stable compounds (such as saturated hydrocarbons). Otherwise oxidation and dehydration occur. A fact to be noted is that very little charring takes place during the heating.

Time did not permit of further experiments with other hydroxy acids being carried out, especially as the results obtained were, on the whole, negative.

University College, Gower Street, W.C.

Dextro-camphorates of Potassium.—E. Jungfleisch and Ph. Landrieu.—The authors have prepared and studied the properties of the following four compounds of potassium and camphoric acid:—Dipotassium *d*-camphorate, monopotassium *d*-camphorate, monopotassium *d*-dicamphorate, and monopotassium *d*-tetra-camphorate. The first of these is very stable and is not decomposed by water, while the others are very unstable in presence of water and decompose to give the dipotassium camphorate and camphoric acid.—*Comptes Rendus*, clvii., No. 19.

COLUMBIUM v. NIOBIUM.

THE Editor has received the following communication and letter from Prof. F. W. Clarke:—

Dear Sir William,—I enclose a brief note which I should like to have inserted in the *CHEMICAL NEWS*. I think English chemists should stand up for their countryman.—Yours sincerely,

F. W. CLARKE.

At a meeting of the Council of the International Association of Chemical Societies in Brussels last September a Committee on Inorganic Nomenclature, among other recommendations, endorsed the name and symbol "niobium" and "Nb" for the element which was originally named columbium. As this recommendation is historically erroneous, a brief statement of the facts appears to be desirable.

In 1801, Hatchett, an English chemist, analysed a strange American mineral, and in it found a new metallic acid; the oxide of an element which he named columbium. A year later, Ekeberg, in Sweden, analysed a similar mineral from Finland, and discovered another element, which he called tantalum. Wollaston, in 1809, undertook a new investigation of these elements, and concluded that they were identical; a conclusion which, if it were true, would have involved the rejection of the later name and the retention of the earlier columbium. The accepted rules of scientific nomenclature make this point clear.

For more than forty years after Hatchett's discovery both names were in current use; for although Wollaston's views were accepted by many chemists there were others unconvinced. In 1844, however, Heinrich Rose after an elaborate study of columbite and tantalite from many localities, announced the discovery of two new elements in them, niobium and pelopium. The latter supposed element was afterwards found to be non-existent, but the niobium was merely the old columbium under a new name. That name in some mysterious manner was substituted by the German chemists for the original appropriate name, and has been in general use in Europe ever since. In America the name columbium has been generally preferred, and was formally endorsed by the Chemical Section of the American Association for the Advancement of Science more than twenty years ago. In England also columbium is much used, as, for example, in Roscoe and Schorlemmer's "Treatise on Chemistry," Thorpe's "Dictionary of Applied Chemistry," and the new edition of the "Encyclopædia Britannica."

The foundation of Rose's error seems to have been an uncritical acceptance of Wollaston's views; for he speaks of all the minerals he studied as tantalite. He also, at least in his original memoir, claims that the atomic weight of niobium is greater than that of tantalum, and here he was obviously wrong.

In short, the name columbium has more than forty years priority, and during that interval was accepted by many chemists, and was more or less in current use. To employ the name niobium is not only unhistorical, but it is also unfair to the original discoverer, meaningless, and without any justification whatever. Furthermore, it injures the splendid reputation of Rose, for it perpetuates and emphasises one of his few errors. The recommendation of the Committee above mentioned should not be accepted, for it is opposed to the established rules of priority.

Fluorine as a Constant Constituent of the Emanations from the Earth's Core.—Armand Gautier.—Fluorine is always found to be present when the following are examined:—The minerals formed in crystalline rocks, thermal springs, emanations from the soil, volcanic gases, and gases from solfaturi. All these products have a very deep-seated origin. Other elements also frequently accompany it, viz., boron, sulphur, nitrogen, arsenic, chlorine, bromine, iodine, silicon, carbon (as CO₂), sodium, free hydrogen, copper, &c.—*Comptes Rendus*, clvii., No. 19.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

APPARATUS FOR TESTING METALS BY IMPINGEMENT
OR SHOCK.

The testing of metals by impingement presents practical difficulties that have been the object of a recent study by MM. G. Charpy and Cornu. These scholars have understood that, in order to obtain a comparison between metallic bars in spite of inevitable local inequalities, it is necessary to impress them with very feeble deformations, very inferior to those that might determine the beginning of a rupture. Tests have been made with a view of discovering if, in operating on un-notched bars, the defect by flexion with the beetle pendulum gave the same identical results, concordant with each other. The tests were made with a beetle or ram-pendulum of 30 kilograms, with a fall of 1.314 metres, and with a pendulum of 300 kilograms, with a fall of 3.197 metres. The relative average error was, in the first case, of 1.4 per 100; in the second case, of 1.0 per 100; that is to say, that the practical identity of the results may be reckoned upon. All the same it is most necessary to take into account the friction against the angular props, and, for both knives and props, to adopt a very rigorously defined form, presenting no acute angles.

STUDIES ON THE RADIO ACTIVITY OF METEOROLOGICAL
WATERS.

A learned physicist, M. Munzo del Castillo, with the help of several collaborators, has effected a certain number of researches concerning the radio-activity of waters of different sources which have led to extremely interesting results. He has remarked that rain-water collected in winter contained a notable proportion of emanation which went on gradually decreasing, as well as a certain quantity of ions that had entirely disappeared at the end of twelve days. Snow that had fallen in Madrid in February also showed a pretty well marked radio-activity. The same physicist has measured the activity of the air of the sub-soil. To extract it he introduced into ditches of two metres deep, at different depths, apparatus formed of a horizontal square surmounted by a cylinder that was filled with little stones and that communicated with the outside by a vertical iron tube; thus at any moment air could be extracted from the sub-soil. The measures and observations taken in autumn have shown that there is no relation between the compared activities of the air of the sub-soil and atmospheric air. The activity of the air of a sub-soil of pretty hard consistence appears to be greater than that of a soft sub-soil. Down to two metres beneath the surface the radio-activity increases with the depth. Other determinations, effected in winter on the compared activities of the air of the sub-soil and of atmospheric air, have enabled it to be observed, besides, that the variations of pressure and of radio activity of the air of the sub-soil are of the same sense as those of atmospheric air, and that the temperature and direction of the wind do not appear to exercise any influence on the radio-activity of the sub-soil. Lastly, M. del Castillo has also taken measures of the radio-activity of several Spanish mineral water springs, and he has noticed a certain activity for the waters of Rivas (Gerona), of Caldas de Juy (Pontevedra), of the Sierra Juansanta (Murcia), and of Garganton (Guadarrama).

METALLIC COATINGS.

M. P. Nicolardot has just made an interesting communication to the Academy of Sciences on the "Actual State of Industrial Metallic Coatings." Of all the processes proposed to obtain metallic coatings on the surface of objects, metallic or not, only three have become

really industrial. They are:—First, dipping into a bath of molten metal; second, electrotyping; third, the Schoop process. M. Nicolardot describes these processes, and shows how they are practised. The only metals with which objects of iron or copper can be plated by a simple dipping are zinc, lead, and tin. The process succeeds only because they form alloys with the underlying metal. The practice of this process requires the employment of considerable quantities of melted metal (as much as 10 cubic metres) in one workshop. This is a cause of very serious accidents that often occur when hollow objects or objects insufficiently dried after scouring are plunged into the melted metal. No way has been found up till the present time to completely suppress these accidents. The process, in spite of the improvements it has received, gives irregular coatings of unequal adherence and thickness. Considerable quantities of metal are consumed, some of it passing into the coating that is always thicker than is necessary, and some into the dross which it partly transforms. Lastly, the working of the process necessitates the employment of a considerable plant, and the temperature of the bath must not exceed 500°; moreover, the plated pieces undergo a second annealing and are sometimes deformed. For all these reasons many trials have been made to obtain metal platings in different manner. Electrolysis only gives a partial solution to the problem, for it can only be performed on objects of rather small dimensions. By this process all the usual metals, excepting lead and aluminium, can be deposited. By different means trials have been made to improve the adherence, the coherence, the compactness, and the regularity of electrolytic deposits, but with only partial success. M. Nicolardot explains the reason of this, and shows the impossibility of obtaining a perfect result. Indeed, the deposit is the result of a veritable bombardment of molecules. They are thrown from one of the electrodes to the other, and their passage is such that the deposits on the planes are always circular or elliptic rings. The superposition of these rings and their displacement gives to the final deposit an alternatively increasing or diminishing thickness, following certain laws, and it is their great number that gives the illusion of their uniformity. The third process, that of Schoop, in its present form consists in projecting violently on to the object the metal for the coating in the form of a very fine powder. For this a pistol is employed. Through this pistol, held in the hand, there is passed a wire of the metal. This wire is heated by an oxyhydric pipe placed within the pistol; then whether the metal has been very strongly heated or whether it has been transformed into a liquid or solid dust, it is driven only by a violent draught, the shaft of which is part of the pistol. The rapid success of this rather new process is explicable by its great convenience and its universality. It can, in fact, be applied to all metals and may be employed to coat all substances, wood, wax, paper, stuffs, lace; it is without danger. Lastly, strange to say, it does not essentially differ from electrolysis. It also acts by bombardment, and the adherence of the deposit can be explained in the same way, as is admitted by M. Nicolardot. In both cases the metal deposited is strongly cold-hammered, and seems to appear in a new allotropic state. M. Nicolardot shows the advantages to be drawn from the porosity of certain deposits obtained by the Schoop process to increase, for example, the resistance to certain corrosive agents; he indicates its application to cementation, to obtain reserves, for the reproduction of mouldings, of phonographic discs, of trichromatic clichés, &c.

SUBTERRANEAN FIRE IN THE COAL FIELDS OF
DECAZEVILLE.

Layers of coal are always in combustion in the coal bed of Decazeville, particularly between that place and Crausac, over a length of about 6 kilometres. At Decazeville in the great basin in which the Commentry-Fourchambault-Decazeville Company, in the open air, works a layer

of 50 metres thick, the least crack in connection with the deep ground sends forth an abundance of smoke. More to the south, at Combes, thirty or forty years ago, the flames issuing from the cracks of the mountains illuminated all the country round during the night. Since then the intensity of this furnace has decreased; nevertheless it is still in activity, the ground is burning hot, and when it rains the mountain is enveloped in mist and steam. A part of the ground to the north of Crausac is called the Etuve (vapour-bath or oven). By digging down into the soil for a dept of 50 centimetres you arrive at an oven of 50°. There was formerly a mineral magnesium spring there, and these natural baths or ovens were employed in the treatment of certain maladies. After the tracing of the galleries of the mines the spring disappeared. However, there is another one of the same kind at Combes. Quite lately, as has been reported by M. G. Patrouilleau, the presence of the subterranean fire to so very far from the surface has been remarked in the town of Decazeville itself. Some workmen who were digging in one of the streets of the town a cutting for laying an armoured cable of 3000 volts, remarked with surprise that, for a length of about 20 metres at about 1 metre's depth, temperature rose to 75° C. The cable was laid, armoured, and isolated by paper, by suspending it in a kennel with lateral chimneys or aeration. From the upper chimney hot air and large quantities of steam come forth. According to the inhabitants of the town this elevation of temperature might have been foreseen, for indeed in the portion of the street under consideration the snow does not lay and the rain water is quickly evaporated. M. Patrouilleau says that from the calcined vestiges found in the basin the fire is in a state of retrogression, but the layers of coal intact are so powerful and so close together that an extension of the scourge, due to subterranean landslips, for example, is always to be feared.

THE ZODIACAL MATTER AND THE SOLAR CONSTANT.

The existence of little intermercurial planets may be revealed by the observation of the perturbations that their masses determine, as well as by the reflection of the solar light and by occultations at periodic intervals. In particular the long periodic inequalities that are to be met with in the theory of the moon may be explained by the existence of a swarm of little intermercurial planets circulating near the sun (Radan, Shint, Blancat). Lastly, the fact that in the month of March the southern edge of comets is brighter than the northern edge, which is further removed from the earth, may be explained by admitting that the zodiacal light represents the elliptic projection of concentric rings crossed by swarms of planets. The passage of these swarms twice a year, in May and November, before the sun seems to be accompanied, according to MM. Abbot, Towle, and Aldrich, by slow and periodic variations of the solar constant, amounting to 5 per 100 in about from seven to ten days.

Colloidal Properties of Meta-hæmoglobin. Modification of Viscosity and Surface Tension of Suspensions by HCl and NaOH.—Filippo Bottazzi.—An aqueous suspension of pure meta-hæmoglobin has about the same viscosity and surface tension as distilled water. When, under the action of HCl or NaOH, the meta-hæmoglobin passes into solution the viscosity of the liquid increases and the surface tension diminishes, the reverse taking place when the acid or alkali is neutralised. When the viscosity has been increased by the addition of HCl it begins to decrease if an excess of acid is added. The addition of sodium chloride produces a small but constant diminution of the surface tension. The lowering of the surface tension depends principally on the undissociated molecules of protein.—*Atti della Reale Accademia dei Lincei*, xxii [ii.], No. 6.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, December 11th, 1913.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"*Intermittent Vision.*" By A. MALLOCK, F.R.S.

When a wheel turns so rapidly that the separate spokes cannot be seen or easily followed by the eye, and if at the same time the observer receives a small mechanical shock of almost any kind, the spokes appear almost stationary for a fraction of a second.

The appearances depend on the speed of rotation, on the brightness of the illumination, and, to a lesser degree, on the nature of the shock.

Suitable shocks are given by the contact of the feet with the ground as in walking by tapping the head or body, and in many other ways.

The convention by which rapid rotation is indicated in drawings, namely, that of introducing a large number of radial lines in place of the actual spokes, probably has its origin in one form of the same phenomenon.

In the paper some experiments are described bearing on the relation between the appearances and the speed of rotation, and an explanation is suggested depending on an assumed variation of sensibility produced by a slight shock. This variation, which it appears is rapidly extinguished, has a periodic time of about 1/18 second, but this differs slightly for different individuals.

"*Attempts to Observe the Production of Neon or Helium by Electric Discharge.*" By Prof. the Hon. R. J. STRUTT, F.R.S.

The present experiments were begun in the hope of confirming the work of Collie and Patterson (*Trans. Chem. Soc.*, 1913, ciii., 419; and *Proc. Chem. Soc.*, 1913, xxix., 217). The results have been negative, whether from a failure to appreciate the proper conditions for the production of neon by electric discharge through hydrogen or from some other cause.

The test for neon was carried out so that the amount found in 1/100 cc. of air could easily be detected.

It was found difficult or impossible to be sure of excluding air, when the hydrogen was pumped out from one apparatus and transferred to another by pneumatic trough manipulation.

This kind of manipulation was avoided. The hydrogen, after each experiment, was converted into water by admitting a little oxygen into the discharge vessel and continuing the discharge for a short time at intervals. The resulting water vapour was frozen out in a side tube cooled by liquid air. Diffusion was free enough to soon remove the whole of it, and a pure oxygen discharge remained. The oxygen could easily be removed by cooled charcoal. Thus the entire series of operations were carried out in one closed apparatus. The discharge with electrodes in a cylindrical tube was tried, both at the cathode-ray stage and at higher pressures; also the electrode-less discharge. The duration of each experiment varied from 8 to 20 hours. In no case was any trace of neon observed.

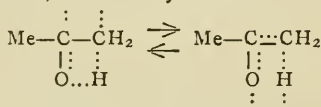
"*The Relations between the Crystal-symmetry of the Simpler Organic Compounds and their Molecular Constitution.*" Part III. By WALTER WAHL.

"*The Selective Absorption of Ketones.*" By Prof. G. G. HENDERSON and I. M. HEILBRON.

Many aliphatic ketones containing one of the groups —CH₂.CO— or —CO.CO—, as well as their derivatives, absorb selectively in the visible and ultra-violet regions. Some at least of them exist in keto and enol modifications, R.CH₂.CO.R' and R.CH:C(OH).R', and according to one hypothesis their absorption is due to some intramolecular vibration which occurs when one tautomeric form changes

into the other. Recent work, however, has shown that aliphatic ketones of the type $R.CO.R'$ are entirely ketonic in form, no trace of an enol modification being present; further, it has been proved that the absorption of ethyl aceto-acetate, which can exist in both forms ($CH_3.CO.CH_2.CO_2Et$ and $CH_3.C(OH):CH.CO_2Et$), is independent of any keto-end oscillation. Hence it is improbable that this form of oscillation is the cause, even indirect, of selective absorption.

The authors have found that the selective absorption of a large number of simple ketones is of the same type, since the absorption bands of all are practically identical. They suggest that the absorption of these compounds may be due to electronic disturbances accompanying oscillations which arise from the alternate formation and breaking down of unstable ring systems within the molecule. For example, the following figures indicate the two phases (each having only a momentary existence) which, according to this suggestion, acetone may assume—



This idea of intramolecular oscillation arising from momentary ring formation can be extended to embrace other groups of ketones, the type of ring formed varying with the constitution of the compound.

"Absolute Measurements of a Resistance by a Method based on that of Lorenz." By F. E. SMITH.

The instrument employed differs from all other forms of apparatus based on the method of Lorenz, inasmuch as two discs are employed instead of one. The disturbing effect of the earth's magnetic field is thus practically eliminated.

The magnetising coils are four in number; they are wound in single layers on marble cylinders, and the disposition of coils with respect to discs is such that the resulting magnetic fields through the discs are opposed in direction, and the intensity of the field at points in the neighbourhood of the edge of a disc is of zero value, or nearly so.

Each of the two discs supports ten insulated bronze segments placed at equal distances around its circumference, and the ten segments on one disc are connected to those on the other disc by ten conducting wires passing through the centre of the shaft. When the wires rotate a difference of potential is produced between their ends. These differences of potential may be placed in parallel or in series and balanced against that on a standard resistance R through which the same current flows as through the coils. The resistance R can thus be found in terms of mutual inductance of coils and brush-contact circles and rate of rotation of conductors.

The brushes consist of thin phosphor bronze wires stretched by spiral springs, and resemble violin bows. Petrol is employed as a lubricant for the brushes. Speed is maintained constant by an electrical method.

The result of the experiments is that a resistance of one international ohm is equal to 1.00052 ± 0.00004 ohms (109cm./sec.).

"A Determination of the Electromotive Force of the Weston Normal Cell in Semiabsolute Volts." By A. N. SHAW. (With a Preface by Prof. H. L. Callendar, F.R.S.)

This paper represents the completion of work commenced by Prof. H. L. Callendar and Mr. R. O. King in the years 1894 to 1898. The E.M.F. of the Weston Cell was balanced against the P.D. on a standard ohm due to a current of about 1 ampere measured by means of an electro-dynamometer of the type described and figured by Clerk Maxwell (*"Electricity and Magnetism,"* vol. ii., p. 339). The original electro-dynamometer proved defective in rigidity of the frame and suspension, and in

insulation of the coils, the dimensions of which could not be measured with sufficient accuracy. The coils were re-wound with a double winding, affording a perfect check on the insulation. The mean radius of the large coils was determined by winding with a measured length of hard-rolled copper tape, graduated on a 50 foot comparator. These coils were also made reversible and interchangeable, in order to eliminate small residual errors of symmetry in determining the mean distance between their planes. The constant of the suspended coils was determined by a null method of comparison with the large coils. A duplex method of reading the deflections was devised, giving an order of accuracy approaching 1 in 100,000. The bifilar suspension was modified so that the control depended mainly on gravity, but there remained a small correction amounting to about 3 parts in 10,000 due to the imperfect elasticity of the suspending wires. The work of reconstructing the apparatus was performed entirely by Mr. King, during 1897-8, under the supervision of Prof. Callendar, who published an account of the preliminary observations made with the apparatus in his paper on "Continuous Electrical Calorimetry" (*Phil. Trans.*, A, 1902, p. 89).

The present author, holding a scholarship endowed by Mr. King, has repeated and verified Mr. King's measurements and results, and has extended the observations and calculations up to the limit of accuracy attainable with the apparatus. In particular, he has been able, by a careful study of Mr. King's suspension (*Phil. Mag.*, 1912), to determine the correction for imperfect elasticity within very narrow limits. The final result for the E.M.F. of the Weston Cell in semi-absolute volts by this method comes out 1.01827 at 20°C. , which agrees closely with the mean of the best recent determinations, namely, 1.01824 . The agreement is of interest because the method presents so many radical points of difference from the majority of those recently employed.

"Elastic Hysteresis in Steel." By F. E. ROWETT.

A thin-walled steel tube was coupled to a coaxial tube of greater section and length. The compound tube was twisted, and the twist in each component measured by spirit levels. The twist of the large tube, in which the stress and therefore also the hysteresis was small, measured the torque applied to the small tube. Strains of the order 10^{-6} were measured in this way, and the energy dissipated by elastic hysteresis during a cycle of stress a little within the elastic limit determined within $2\frac{1}{2}$ per cent. The dissipation was observed when the same tube was subjected to similar stress cycles at a rate of 60 per second. For this purpose the tube was fixed at one end, a fly-wheel mounted on the other, and the rate of decay of torsional oscillations was observed photographically. The energy dissipated per cycle was found to be the same as in the static experiment. The elastic hysteresis in hard drawn tubes was about one-eighth of that in the same tube after annealing.

"A Simple Form of Micro-Balance for Determining the Densities of Small Quantities of Gases." By F. W. ASTON.

1. A simple micro-balance is described, by which the densities of gases may be determined relative to some standard gas, using a null method.

2. About half a cubic centimetre only of the gas is required.

3. The determination can be performed in a few minutes, with an accuracy of 0.1 per cent.

4. Possibilities of its use in other fields of research are indicated.

"On a Second Spectrum of Neon." By F. R. MERTON.

The Spectrum of Neon has been investigated under different conditions of electrical excitation. It has been found that with a condensed discharge a second spectrum is developed, as in the case of Argon, Krypton, and Xenon. The strongest lines of the ordinary spectrum are also feebly visible when a condensed discharge is used.

CHEMICAL SOCIETY.

Ordinary Meeting, November 6th, 1913.

Prof. W. H. PERKIN, LL.D., F.R.S., President,
in the Chair.

(Concluded from vol. cviii, p. 317).

274. "The Action of Chlorine on *m*-Iodoaniline and on *m*-Bromoaniline." By HAMILTON McCOMBIE and PERCY JAMES WARD.

When *m*-iodoaniline is chlorinated in glacial acetic acid solution, 2 : 4 : 6 trichloro-3-iodoaniline is produced. Under no conditions could an iododichloride be obtained; this is contrary to the experience of Willgerodt and Wikander (*Ber.*, 1907, xl., 4068), who considered that they obtained an unstable iododichloride. When 2 : 4 : 6-trichloro-3-iodoaniline is treated with alcoholic ethyl nitrite, 2 : 4 : 6-trichloroiodobenzene is produced, which has been described previously by several observers. 2 : 4 : 6-Trichloro-3-iodoaniline could not be converted into a hydrochloride, nor could it be benzoylated in presence of sodium hydroxide.

The acyl derivatives of *m*-iodoaniline showed a slight tendency to the formation of iododichlorides, but these proved to be very unstable, and readily yielded ring substitution products.

The prolonged action of chlorine on *m*-iodoaniline resulted in the formation of 2 : 2 : 3 : 4 : 4 : 6 hexachloro-5-iodo-Δ⁵-cyclohexenone, $\text{CCl}_2 < \begin{smallmatrix} \text{CHCl} \\ \text{Cl} \end{smallmatrix} \text{CCl}_2 > \text{CO}$. In this reaction the amino-group has been removed in the form of ammonium chloride, whilst the iodine atom still remains in the molecule. The constitution of this ultimate chlorination product is based on the following reactions:—1. On treatment with potassium iodide, the compound yields 2 : 4 : 6 trichloro-3-iodophenol. 2. On treatment with potassium acetate in the presence of acetic acid, these results 2 : 3 : 4 : 6-tetrachloro-5-iodophenol. 3. Concentrated sulphuric acid converts the compound into 2 : 3 : 6-trichloro-5-iodo *p*-benzoquinone.

Analogous results have been obtained on chlorinating *m*-bromoaniline under the same conditions as were employed for the iodo-compound.

275. "Guanidinium Nitrite and its Decomposition by Heat." By PRAFULLA CHANDRA RAY, MANIK LAL DEY, and SARAT CHANDRA JANA.

Guanidinium nitrite, from the conductivity measurement of its aqueous solution, is found to behave like a typical alkaline nitrite with two ions.

When heated, guanidinium nitrite yields ammonia, hydrocyanic acid, nitrogen monoxide, and nitrogen among the gaseous products, and leaves a residue which was proved to be melamine.

276. "The Absorption of Light by Uranous Chloride in Different Solvents." By THOMAS RALPH MERTON.

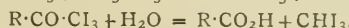
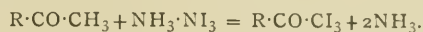
The absorption spectra of uranous chloride solutions in different solvents have been investigated, more especially in the presence of free hydrogen chloride. In some cases the presence of a small quantity of water produces a marked change in the absorption spectrum. It is concluded that the vibrators responsible for different bands or groups of bands are situated in different molecular aggregates.

277. "The Influence of Solvents on the Rotation of Optically Active Compounds. Part XIX. The Rotation of certain Derivatives of Lactic Acid." By THOMAS STEWART PATTERSON and WILLIAM COLLINS FORSYTH.

The rotation of several derivatives of lactic acid has been examined, over a range of temperature, both in the homogeneous state and in solution in two solvents, which usually differ widely in their action.

278. "The Action of Nitrogen Iodide on Methyl Ketones." By FREDERICK DANIEL CHATTAWAY and ROBERT REGINALD BAXTER.

Ketones containing a methyl group react very readily with nitrogen iodide, iodoform, ammonia, an acid, and an amide being formed. In the reaction the methyl group appears to be completely substituted by iodine, a tri-iodomethyl ketone being formed, which in presence of the ammonia simultaneously set free is hydrolysed to iodoform and an acid. A similar reaction between the substituted ketone and ammonia leading to the formation of iodoform and an amide. The reactions may be formulated thus:—



The reaction between nitrogen iodide and acetone is particularly striking, as the black solid in a few minutes is apparently transformed into a bright yellow one.

279. "Note on the Constituents of Commercial Chrysarobin." By FRANK TUTIN and HUBERT WILLIAM BENTLEY CLEWER.

In a recent communication (*Trans.*, 1912, ci., 290) the authors described the results of the examination of several samples of commercial chrysarobin. During the course of this research the following substances were isolated:—Chrysophanol ("chrysophanic acid"), $\text{C}_{15}\text{H}_{10}\text{O}_4$; emodin monomethyl ether, $\text{C}_{16}\text{H}_{12}\text{O}_5$; chrysophanolanthranol, $\text{C}_{15}\text{H}_{12}\text{O}_3$; dehydroemodinanthranol monomethyl ether, $\text{C}_{16}\text{H}_{12}\text{O}_4$; arabinol, $\text{C}_{23}\text{H}_{16}\text{O}_5$; and emodin, $\text{C}_{15}\text{H}_{10}\text{O}_5$.

It was furthermore pointed out that commercial chrysarobin is subject to considerable variation in the relative proportions of its constituents, some samples being even entirely devoid of certain compounds which occur in others. In all the products examined, however, the first four of the above mentioned compounds were invariably found to be present.

Very shortly after the appearance of the above communication a paper on the same subject was published by O. Hesse (*Annalen*, 1912, cccxxxviii., 65). The results described in the latter paper, however, are such as would give the impression, at first sight, that the conclusions of Hesse and those of the present authors had very little in common. Some further explanation of the subject therefore appears desirable.

Hesse mentions as constituents of commercial chrysarobin the following substances:—"Chrysophanol" (see Note) (chrysophanolanthranol); "emodinol" (emodinanthranol); the methyl ethers of both these substances; and a new substance, $\text{C}_{15}\text{H}_{12}\text{O}_4$, which is designated as chrysarobol. It is stated by Hesse, however, that of these five substances, only two, namely, "chrysophanol" (chrysophanolanthranol) and chrysarobol, had been isolated directly in a pure state from commercial chrysarobin, whereas all the constituents described by the present authors were directly isolated in a state of purity.

(NOTE.—It would appear unfortunate that Hesse should have employed the name chrysophanol for the anthranol of "chrysophanic acid," since the former name had already been employed by the present authors (*loc. cit.*, p. 292), and previously by Tschirch (*Arch. Pharm.*, 1911, cclxix., 222, and 1912, ccl., 27), as the designation for pure "chrysophanic acid." Moreover, since Hesse himself (*Annalen*, 1899, cccix., 32) and Jowett and Potter (*Trans.*, 1902, lxxxi., 1577) have previously applied the name "chrysarobin" to chrysophanolanthranol, the employment of yet a third name for this substance only adds to the confusion already existing).

Chrysophanolanthranol has long been known to be a constituent of commercial chrysarobin, but chrysarobol has not been obtained by the present authors. This is doubtless due to the varying composition of the com-

mercial product, since Hesse remarks that he only obtained this new substance from the chrysarobin occurring in commerce in the years 1905 and 1906.

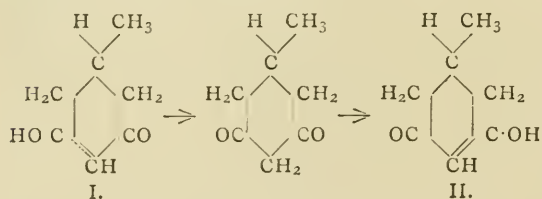
With regard to emodinanthranol (Hesse's "emodinol"), no doubt can be entertained that this was derived chiefly from the monomethyl ether of dehydroemodinanthranol (see Note) which was isolated and described by the present authors, since the material examined by Hesse had been heated with hydriodic acid. Hesse himself shows that he could not obtain "chrysophanol methyl ether" and "emodinol methyl ether" in a state of purity, and the evidence he adduces does not seem to justify the conclusion that they are present. In the material examined by the present authors, the former compound certainly did not occur, but proof of the presence of small amounts of the latter was obtained.

The statement made by Hesse that chrysophanol-anthranol (Hesse's "chrysophanol") is insoluble in alkalis in the absence of air is incorrect. This substance dissolves fairly readily in 10 per cent aqueous potassium hydroxide, yielding a bright yellow solution, which, on the admission of air, develops the deep red colour due to the formation of chrysophanol.

(NOTE.—In a footnote to his paper, added after the completion of the work, Hesse states that he has never observed the occurrence of the monomethyl ether of dehydroemodinanthranol described by the present authors, but this is obviously due to his having worked almost entirely with material which had been demethylated by means of hydriodic or hydrochloric acid. In all the commercial samples of chrysarobin examined by the present authors it was present to the extent of from 13.4 to 41.1 per cent).

280. "Substituted Dihydroresorcins. 1-Methyldihydroresorcin and 2-Methyldihydroresorcin." By CHARLES GILLING.

1-Methyldihydroresorcin is a tautomeric substance, and it is suggested that this tautomerism prevents the existence of the two stereoisomeric forms, since it is apparent that I. and II. are mirror images of each other :—

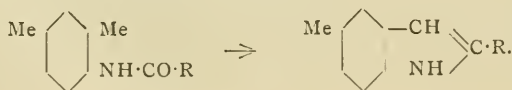


The replacement of the labile hydrogen atom by an ethyl group destroys this tautomerism, and the ethyl ether can accordingly be isolated in two distinct forms.

2-Methyldihydroresorcin can be prepared from cresorcinol by reduction, but the product so obtained is impure, and it was only isolated in the form of crystalline derivatives.

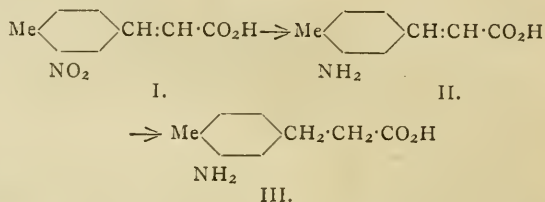
281. "Researches on the Constitution of Physostigmine. Part III. The Formation of Substituted Indoles from m-4-Xylidine, and the Reduction of 3-Nitro-p-tolylacrylic Acid." By ARTHUR HENRY SALWAY.

In this investigation the author has described some experiments, which were conducted with the object of ascertaining whether Madelung's reaction for the preparation of substituted indoles from o-toluides (*Ber.*, 1912, xlv., 1128, 3541) could be applied to acyl derivatives of m-4-xylidine, according to the scheme :—



It has now been shown that aceto-m-4-xylidide readily yields 2:5-dimethylindole by this method. The reaction, however, was found not to be generally applicable since 2:4-xylilsuccinamic acid, $C_6H_3Me_2 \cdot NH \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$, and its derivatives, which were of interest in connection with the problem of the constitution of physostigmine, could not be converted into indoles without disruption of the molecule.

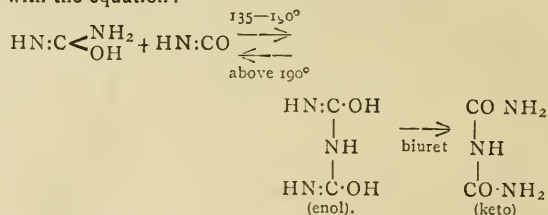
The reduction products of 3-nitro-p-tolylacrylic acid (I.) have also been described. It has been ascertained that the nitro group of this substance is more readily attacked by reducing agents than the cinnamyl residue, so that the first product of the reaction is 3-amino-p-tolylacrylic acid (II.), which by further reduction is converted into 8-3-amino-p-tolylpropionic acid (III.):—



282. "Mechanism of the Decomposition of Carbamide and Biuret by Heat, and of the Formation of Ammelide." By EMIL ALPHONSE WERNER.

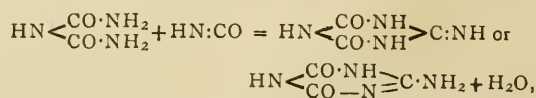
In continuation of work recently published (*Trans.*, 1913, ciii., 1010), a quantitative study of the decomposition of carbamide and biuret by heat has been made, the results of which have thrown new light on the mechanism of the progressive changes.

It was shown that the formation of biuret by the action of heat on carbamide is a reversible reaction in accordance with the equation :—



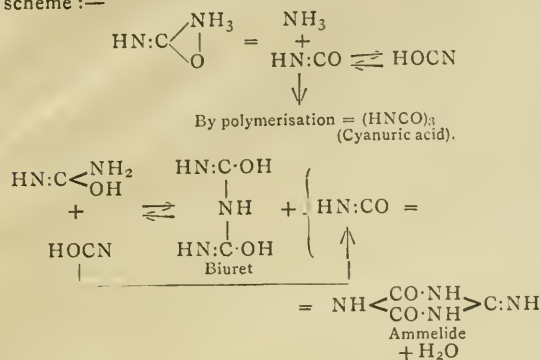
By heating pure anhydrous biuret for five minutes at 192° (m. p. 190°), as much as 30 per cent of regenerated carbamide was extracted from the residue. The general idea that biuret decomposes directly into ammonia and cyanuric acid is therefore erroneous.

No evidence could be obtained of the formation of tri-cyanocarbamide, $C_3N_3(NH \cdot CO \cdot NH_2)_3$, described by Hantzsch and F. Hofmann (*Ber.*, 1905, xxxviii., 1010) as a product of the action of heat on carbamide; the properties of the substance described by them are identical with those of ammelide (cyanuric monamide), which has been long since recognised by Liebig and Wöhler and others as a product of the decomposition of carbamide. Proof was obtained that this compound originates from the further interaction of cyanic acid and biuret according to the equation :—



and hence is also formed during the decomposition of biuret, but in smaller quantity, since the conditions are less favourable. Thus it was shown that the whole cycle of changes which take place during the decomposition of carbamide and biuret by heat can be simply explained by

(1) dissociation, and (2) instability and reactivity of nascent cyanic acid, as illustrated by the following scheme:—



283. "Note on the Mechanism of a Bromination in Ketones." By ARTHUR LAPWORTH.

H. Leuchs has recently found that, by bromination of an optically active ketonic acid, a monobromo-derivative is obtained which exhibits some optical activity. As the activity of both compounds is dependent on enantiomorphism in the arrangement of the atoms and groups around the α -carbon atom to which the bromine attaches itself, Leuchs concludes that the enolic form of the ketone could not have been an intermediate stage in the substitution process, and he suggests applying a similar test to active monalkylmalonic hydrogen esters (*Ber.*, 1913, xlv., 4238).

Leuchs's inference is not quite conclusive, for the facts admit of different interpretations; for example, if the ketonic acid, like other carboxylic acids, is to any extent associated, and substitution takes place in one part of a polymolecule only, then the remainder of the polymolecule may retain its enantiomorphous arrangement during enolisation of the first portion, and consequently the formation of a new "asymmetric" carbon atom in the latter would naturally lead to the formation of some excess, however small, of atoms of one sign. In other words, a "partial asymmetric synthesis" is possible.

The bromination of active α -methylbutyric acid has previously been studied by Schütz and Marckwald (*Ber.*, 1896, xxix., 59), and of β -phenylisobutyric acid by Lapworth and Lenton (*Proc.*, 1902, xviii., 35). In both instances the product was inactive.

284. "Studies in the Diphenyl Series. Part V. Derivatives and Substitution Products of the Two Isomeric *o*-Dinitrobenzidines and Synthesis of Derivatives of Benzerythrene." By JOHN CANNELL CAIN, ALBERT COULTHARD, and FRANCES MARY GORE MICKLETHWAIT.

The authors have prepared a number of acyl and azo-derivatives of the two isomeric *o*-dinitrobenzidines (*Trans.*, 1912, ci., 2298), and have submitted the two bases to the diazo-reaction.

3:3'-Dinitrobenzidine gives the corresponding disubstituted 3:3-dinitrodiphenyl, but 3:5'-dinitrobenzidine, in those cases where copper is employed, gives derivatives of benzerythrene:—



Of the numerous derivatives of the two bases that have been prepared, no two corresponding ones are identical.

285. "Harmin and Harmaline. Part II. The Synthesis of iso-Harman." By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

A detailed description of work of which a preliminary account has already appeared (*Proc.*, 1912, xxviii., 154).

NOTICES OF BOOKS.

Researches on Irritability of Plants. By JAGADIS CHUNDER BOSE, M.A., D.Sc., C.S.I. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

THE experiments described in this book are exceedingly interesting, and the author appears to have arrived at results of vital importance in biochemistry. He has devised and perfected two pieces of apparatus which he calls the Resonant and Oscillating Recorder respectively, by means of which the amplitude and period and also the absolute rate of movement of the plant during any phase of autonomous response to stimulation can be determined with perfect accuracy. He has found it possible to record time-intervals which do not exceed one-thousandth of a second in length. The so-called sensitive plants were chosen for study, and mechanical, chemical, thermal, and electrical methods of stimulations were included. The general result of the experiments is the revelation of a remarkable similarity of response in the plant and the animal.

Practical Sanitation. By GEORGE REID, M.D., D.Ph. Seventeenth Edition. London: Charles Griffin and Co., Ltd. 1913.

ALTHOUGH it is only eighteen months since the sixteenth edition of this book was published, progress in sanitation has been so rapid that in the eighteenth edition a good many alterations and additions have been found necessary. The book gives a thoroughly practical outline of the elements of sanitation, and inspectors, builders, and plumbers, medical officers of health, and householders will find it full of valuable information. The appendix on English sanitary law will serve as a useful guide to the reading of candidates for examinations on the subject.

The Application of Physico-chemical Theory to Technical Processes and Manufacturing Methods. By Prof. Dr. R. KREMANN. Translated from the German by HAROLD E. POTTS, M.Sc. (Liverpool), and Edited by ALBERT MOND, Ph.D. London: Constable and Co., Ltd. 1913.

THE value of a knowledge of physical chemistry to the enlightened technical chemist who is anxious to keep abreast of the times and to shake himself free from the bondage of rule-of-thumb methods is fully recognised on all sides, and in spite of the difficulty of the subject it is most necessary that the student should get an early acquaintance with it, so that when he approaches more advanced work in his own special branch he should be able to do so from the physico-chemical standpoint. This book gives a useful introduction to the subject. The chapters are graduated in difficulty, and a minimum amount of mathematics is introduced. Many industries are adequately dealt with, and the phase rule is particularly clearly explained and illustrated. The translation has been carefully done and the book is well printed; the only error which a careful examination has brought to light being in the lettering of the diagram of a gas-engine, where the illustration does not agree with the text.

Industrial Research in America. Presidential Address. By ARTHUR D. LITTLE. Reprinted from the *Journal of Industrial and Engineering Chemistry*. 1913.

THIS Presidential Address, delivered before the American Chemical Society, gives a very stimulating account of the state of industrial research in America, and contains some remarkable facts and figures concerning the development of certain industries and the solution of some technical problems by American chemists. The research work done by the ten great scientific bureaus organised and controlled by the Department of Agriculture has led to results of great value, some of which are briefly summarised in the address, and short accounts are also given of the pioneer work in industrial research which is being

done by some of the Universities and technical schools. The words of the President regarding the applications of chemical science to the industries in the future are so generally applicable that they are well worth quoting:—"We shall need for years to prosecute a vigorous campaign for a better understanding by the general public of what chemistry is and what research is. The popular imagination is ready to accept any marvel which claims the laboratory as its birthplace, but the man in the works still disbelieves that two and two in chemical nomenclature make four. We need a multiplication of research laboratories in special industries, each with an adequate staff of the best men obtainable and an equipment which gives full range to their abilities."

Die Chemische Verwandtschaft. ("Chemical Affinity"). By Dr. MAX SPETER. Leipzig: Philipp Reclam, jun. 1913. (80 Pf.).

THIS booklet deals with the connection between chemical affinity and thermic, electric, and radiant energy, and gives a short summary of the experimental data which have been collected and the general laws which have been deduced from them. The author does not put before his readers many speculations as to the nature of the force which brings about the combination of substances, but confines himself to the statement of the positive results which have been obtained, and considering the very small size of the book he does so with great completeness and clearness.

Whitaker's Almanac for 1914. Half Bound, 904 pages. J. Whitaker and Sons.

A LIST of some thirty-five new features are given as having been introduced in this issue, enough to show that the publishers are fully determined to maintain the reputation of the almanac. Among the items we note the Home Rule Bill, Royal Flying Corps, Labour Unrest, Aeronautics, National Health Insurance Amendment Act, Wireless Telegraphy, and other current topics. "Whitaker's Almanac" is too well known to require further introduction: we need only say that it is as good as ever.

Whitaker's Peerage, Baronetage, Knightage, and Chivalry for 1914.

DURING the past year Honours appear to have been distributed somewhat more sparingly than of late, and the Obituary list is ominously long. A great deal of interesting and useful information is given in the way of footnotes, in addition to the official matter. Amongst other things we note that much of the fable and superstition connected with the Coronation Stone, so well known to all visitors to the Abbey, has been cleared away by Sir Archibald Geikie, who, speaking as a geologist, declares that the stone was almost certainly quarried in the sandstone district between Argyll and the Forth. An interesting account is given of the ceremony of the Coronation of the present King, together with many quaint observances not generally known.

CORRESPONDENCE.

INSTITUTE OF CHEMISTRY CONFERENCE.

To the Editor of the Chemical News.

SIR,—As one who has criticised the ways of the Institute of Chemistry, I am glad to see that there is a decided opinion among teachers of chemistry that this Society might be improved.

I would suggest that it would be in its best interests to abolish the practical examinations altogether. To suggest that any examiners can tell whether a man is a competent chemist by working in a strange laboratory for six hours or so a day for three or four days, under conditions that are never found in practice, seems to me a very unscientific way of finding out a man's capabilities. The exercises set

are frequently open to criticism as to whether an analyst could do them in the time allowed, even in one's own laboratory. The large percentage of failures show there must be something wrong.

As an alternative to practical examinations, suppose the Institute insisted upon a two years course of general chemistry in a college, or a three years course at evening classes, and then made each student analyse correctly a series of salts the composition of which was known only to a small examining committee. The diploma not to be given until the series were correctly analysed. This might take two or four or more years, either at a day college or evening classes. I do not mean the same series for every student.

I am sorry to see the attitude taken up by some gentlemen, that class distinctions have anything to do with abilities. There are chemists in this country who have had to make the best use they could of the limited opportunities for learning which they could afford, and whose opinion would now be taken in preference to a F.I.C. in cases of dispute, but if any of these gentlemen applied under the terms of the Charter for election to the Fellowship they would probably be told that "their qualifications are not such as would justify the Council in admitting them to the F.I.C.," and probably, without any disrespect, not one of the Council would be equal to them scientifically in their special branches.—I am, &c.,

ERNEST A. LEWIS.

310, Dudley Road, Birmingham,
December 20, 1913.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances des l'Académie des Sciences. Vol. clvii., No. 19, November 10, 1913.

Origin of Cyclic Bases of Coal-tar.—L. C. Maillard. —The cyclic bases of tars undoubtedly derive their nitrogen from ancient protein material, and according to the author's view the intermediate products are nitrated humic matter resulting from the condensation of the sugars (constituents of cellulose, &c.) with amino-acids (constituents of proteins). The formation of volatile bases at the expense of the humic matter is due to pyrogenation, but it is certain that the union of the amino-nitrogen with the carbon chain of the sugars occurs before pyrogenation.

Decomposition of Halogen Alkylates of Hexamethylene-tetramine. — Marcel Sommelet. — Boiling water is capable of decomposing the halogen alkylates of hexamethylene-tetramine, particularly those which are derived from benzyl chloride and analogous compounds. The somewhat unexpected result is the formation of the aldehyde of the halogen derivative. The chlorobenzylate is so sensitive to the action of water that benzoic aldehyde is obtained by simply heating its solution in aqueous alcohol. The bromotolulylates of hexamethylene-tetramine are similarly transformed into toluic aldehydes.

MEETINGS FOR THE WEEK.

- MONDAY, 5th.—Society of Chemical Industry, 8. "Viscosity of Oils," by J. L. Strevens. "Oxygen Content of Gases from Roasting Pyrites," by Lewis T. Wright. "Electrical Conductivity of Milk during its Concentration, with suggestions for a Practical Method of Determining the End-point in the Manufacture of Sweetened Condensed Milk," by L. C. Jackson, Leslie McNab, and A. C. H. Rothera. "Monazite from some New Localities," by S. J. Johnstone.
- TUESDAY, 6th. { Royal Institution, 3 (Christmas Lectures, adapted to a juvenile auditory). "A Voyage in Space," by Prof. H. H. Turner.
- THURSDAY, 8th. {
- WEDNESDAY, 7th.—Royal Society of Arts, 5. (Juvenile Lecture. "Electric Vibrations and Wireless Telegraphy)" by R. P. Howgrave-Graham, M.I.E.E.

THE CHEMICAL NEWS.

VOL. CIX., No. 2824.

THE DIMETHYL PHOSPHATES OF THE RARE EARTHS.*

By J. C. MORGAN AND C. JAMES.

THE study of methods for the separation of the rare earths and of new compounds of the rare earths that seem likely to be of use for such purposes has for a long time occupied the attention of those interested in this branch of chemistry.

The rare earth salts of dimethyl phosphoric acid seemed, on preliminary investigation, to be possessed of properties which would make dimethyl phosphoric acid an extremely valuable reagent for the separation of some of the rare earths. Therefore a study of the properties of these compounds was commenced.

This investigation involved the preparation of dimethyl phosphoric acid; the preparation of the rare earth compounds from this; the determination of the composition and solubility of these compounds; and, finally, several fractionations of rare earth mixtures.

Preparation of Dimethyl Phosphoric Acid.—This acid was prepared, according to the method of Hugo Schiff (*Chem. Central Blatt*, 1857, 761—763, 864), by allowing methyl alcohol to drop slowly into phosphorus oxychloride. About 200 cc. of phosphorus oxychloride were placed in a litre flask, and 250 cc. of methyl alcohol were added, drop by drop, through a separatory funnel fitted to the flask. During the reaction the flask was shaken in a stream of cold water, and the temperature maintained between 25° and 30°. The large quantities of hydrochloric acid gas and methyl chloride which were evolved passed off through a side tube. At the completion of the reaction, which required from an hour to an hour and a-half, there remained a colourless somewhat syrupy liquid, consisting of both dimethyl phosphoric and phosphoric acids with some hydrochloric acid and methyl chloride. This was removed to an evaporating dish, and heated upon the steam-bath until the hydrochloric acid and methyl chloride were expelled. The syrupy acids were then diluted and neutralised with barium carbonate. The phosphoric acid was removed as barium phosphate. The precipitate was filtered off, leaving a clear filtrate consisting of a solution of barium dimethyl phosphate, together with traces of barium monomethyl phosphate. This solution was treated with just sufficient sulphuric acid to precipitate all the barium as the sulphate, which after digestion at 95° was removed by filtration, leaving a clear solution of dimethyl phosphoric acid.

Yttrium Dimethyl Phosphate.—This salt was obtained by dissolving yttrium hydroxide in dilute dimethyl phosphoric acid. After stirring for some time the liquid became clear. The solution was then filtered and placed upon a water-bath, the temperature of the latter being kept at about 90°. This treatment caused a quantity of crystalline yttrium dimethyl phosphate to form. The precipitate was filtered off and washed with boiling water. The compound was next dissolved in as small an amount of water as possible, and permitted to crystallise by spontaneous evaporation. Groups of white needle-like crystals, radiating from a common centre, were formed. These were removed, dried between filter-papers, and then placed in an oven at 100° for four hours. The results of the analysis seemed to show that a very small amount of water was retained. Further drying at the same temperature failed to make any difference.

Yttrium dimethyl phosphate dissolves in water at 25° to

the extent of 2.80 parts of the anhydrous salt to 100 parts of water. At 95° only about 0.55 part dissolve in 100 parts of water.

Y_2O_3 ; calculated, 24.34; found, 24.06.

Lanthanum Dimethyl Phosphate.—This substance was prepared by dissolving the oxide in dilute dimethyl phosphoric acid. The solution, after filtration, was concentrated upon a water-bath until a skin began to form upon the surface, after which it was permitted to crystallise by spontaneous evaporation. The resulting crystals were dissolved in water and re-crystallised once again by spontaneous evaporation. These crystals were separated from excess of mother-liquor by pressing between filter-papers, and finally dried in air.

Lanthanum dimethyl phosphate forms white hexagonal crystals. One hundred parts of water dissolve 103.7 parts of the anhydrous salt at 25°. The solubility at 100° did not vary like the other rare earths. The solubility at 95° appeared to be somewhat difficult to obtain owing to the fact that the solution had a tendency to become colloidal.

In order to determine the phosphorus a weighed sample of lanthanum dimethyl phosphate was first fused with sodium peroxide to oxidise the methyl groups and get the phosphorus present as phosphate. The usual method was then followed.

Calculated: La_2O_3 , 29.63; P_2O_5 , 38.75. Found: La_2O_3 , 29.45; P_2O_5 , 38.63.

From the above analysis it was considered that the compound contained 4 molecules of water of crystallisation, as shown by the formula $\text{La}_2[(\text{CH}_3)_2\text{PO}_4]_6 \cdot 4\text{H}_2\text{O}$.

Cerous Dimethyl Phosphate.—The cerous compound was obtained by treating cerous carbonate with a dilute solution of the acid. The clear solution was evaporated on the water-bath until a skin began to form upon the surface, as was observed in the case of the preceding substance. It was further concentrated by spontaneous evaporation. The crystals obtained in this manner were again crystallised from water.

Cerous dimethyl phosphate is a white crystalline solid belonging to the hexagonal system. It is very soluble in cold water, but less soluble in hot. One hundred parts of water dissolve 79.6 parts of the anhydrous salt at 25° and about 65 parts at 95°. Upon analysis 33.08 per cent CeO_2 was found. This still remained after drying for some time at 100°, and corresponded to the formula $\text{Ce}_2[(\text{CH}_3)_2\text{PO}_4]_6 \cdot \text{H}_2\text{O}$.

Praseodymium Dimethyl Phosphate.—A solution of this dimethyl phosphate was prepared by dissolving praseodymium oxide in the acid. The liquid was concentrated on the water-bath until small crystals began to form, after which it was set aside to evaporate at ordinary temperatures. The compound purified by re-crystallisation formed green hexagonal crystals. 64.1 parts were dissolved by 100 parts of water at 25°.

Neodymium Dimethyl Phosphate was prepared in a similar manner to the praseodymium compound. It forms pale lilac coloured hexagonal plates. At 25°, 56.1 parts dissolve in 100 parts of water, while at 95° only about 22.3 parts are dissolved by 100 parts of water. An analysis showed the presence of 32.27 per cent of Nd_2O_3 , thus pointing to the formula $\text{Nd}_2[(\text{CH}_3)_2\text{PO}_4]_6$.

Samarium Dimethyl Phosphate.—A small quantity of the acid was neutralised with samarium oxide. The solution thus obtained was concentrated on the water-bath until nearly solid, owing to the formation of the dimethyl phosphate crystals. It was filtered while still hot. The salt was dissolved in water and crystallised by evaporation at ordinary room temperature.

Samarium dimethyl phosphate forms cream coloured hexagonal prisms. One hundred parts of water dissolve 35.2 parts of the salt at 25° and about 10.8 parts at 95°. 33.11 per cent Sm_2O_3 was found to be present, indicating no water of crystallisation like most of the rare earth dimethyl phosphates.

* Contribution from the Chemical Laboratories of New Hampshire College.

Gadolinium Dimethyl Phosphate was separated from its solution by carefully heating.

It forms white needle-like crystals very similar to the yttrium compound. One hundred parts of water dissolve 23.0 parts of the salt at 25°, while only 6.7 parts are dissolved by the same quantity at about 95°. The compound contained 34.00 per cent Gd_2O_3 .

Erbium Dimethyl Phosphate was prepared in a similar way to the yttrium salt described below.

It forms very pale coloured needles, 1.78 parts dissolving in 100 parts of water at 25°.

Ytterbium Dimethyl Phosphate.—The ytterbium oxide was dissolved in a slight excess of hydrochloric acid and the solution diluted considerably. A sufficient quantity of dimethyl phosphoric acid to react with the ytterbium present was neutralised with sodium carbonate, and then made slightly acid with a few drops of dimethyl phosphoric acid. This solution was diluted and slowly added to the ytterbium chloride with careful stirring. A precipitate of ytterbium dimethyl phosphate formed, which slightly increased in amount on heating the solution to 100°. The precipitate was filtered off, dissolved in cold water, and again precipitated by heating. The white needle-like crystals dissolve to the extent of 1.2 parts per 100 parts of water at 25°. Only 0.25 are dissolved by 100 parts of water at about 95°. An analysis showed 35.73 per cent Yb_2O_3 , which corresponds to the amount contained in the formula of the anhydrous substance.

Table of Solubilities of Dimethyl Phosphates.

Element.	Crystal form.	Parts of salt per 100 parts of water at 25°.
Lanthanum	Hexagonal crystals	103.7
Cerium	" plates	79.6
Praseodymium	" "	64.1
Neodymium	" "	56.1
Samarium	" prisms	35.2
Gadolinium	Long needles	23.0
Yttrium	" "	2.8
Erbium	" "	1.78
Ytterbium	" "	1.2

Fractionation of Material.—Since, as already stated, the study of new compounds of the rare earths is carried on mainly to obtain compounds adaptable to a more complete and more rapid separation of these elements, no study would be complete without determining the behaviour of mixtures of the dimethyl phosphates. Several fractionations were conducted, and the method employed was that of precipitation by heat, in the case of the less soluble compounds a dilute solution was prepared. The beaker containing this solution was then placed in a water-bath and the temperature of the bath gradually raised, the solution being constantly stirred. As soon as a fair amount of precipitate had formed, the liquid was filtered off and the precipitate retained as fraction I. The filtrate was again heated until another lot had separated and again filtered. The dimethyl phosphates collected from this second heating were put aside as fraction II. In this manner fractions were taken up to and inclusive of 95°. Additional fractions were obtained by fractionally evaporating the mother-liquor.

These fractions were further fractionated by dissolving the least soluble fraction in water, and heating in the water-bath to the temperature at which fraction I. was removed. The precipitate which had formed at this point was removed by filtration and retained as fractions I.—II. The filtrate was used to dissolve fraction II., and the solution heated as before to the temperature of removal of fraction II. The precipitate was taken as fraction II.—2, and the filtrate used to dissolve fraction III. By proceeding in this manner any degree of fractionation which was desired could be obtained.

During and at the completion of the fractionation various fractions were examined with regard to colour of oxide, nitric acid solution, and spectrum.

Gadolinium Material.—A material containing gadolinium with only sufficient traces of terbium to colour the oxide orange-brown was first submitted to fractionation with dimethyl phosphoric acid.

The oxide of this crude gadolinium was dissolved by stirring with the acid until all had dissolved. The liquid was then treated as described above.

The fractions were taken as follows:—Fractions I., I.—2, I.—3 at 65°; fractions II., II.—2, II.—3, at 90°; fractions III., III.—2, III.—3, after evaporating the mother-liquor from fractions II. to one-half volume; and fractions IV., IV.—2, IV.—3 upon complete evaporation.

A fair idea can be formed with regard to the rapidity of the method by observing the change in colour of the oxides. The oxide from fraction II. was of a dark brown colour; that of fraction IV. light brown, and that of fraction IV.—3 pale cream.

This showed a rapid concentration of the gadolinium in the most soluble fractions, while the impurity—terbium—collected in the least soluble.

It is interesting to note that this fractionation required only about forty-eight hours to give a comparatively pure gadolinium. This shows a great increase in the rapidity of the separation over all previous methods.

Fractionation of Yttrium Material.—The next oxides consisted of a mixture of those of yttrium, holmium, and dysprosium with traces of erbium, samarium, gadolinium, terbium, neodymium, and praseodymium. They were dissolved in hydrochloric acid, the solution diluted and boiled with an excess of sodium hydroxide. The precipitated hydroxides were filtered off, washed with hot water until free from chlorides, and dissolved by stirring with the dilute dimethyl phosphoric acid. The resulting solution was then submitted to the usual fractionation.

Fraction I. was removed at 38°, fraction II. at 48°, fraction III. at 65°, fraction IV. at 96°, while fractions V., VI., VII., and VIII. were taken by fractionally evaporating the mother-liquor from fraction IV.

Fraction I.—The oxide was yellowish, and the absorption spectrum showed a rapid concentration of erbium. Holmium and dysprosium were also present.

Fraction II.—This portion gave a yellowish coloured oxide. The spectroscopic showed holmium and dysprosium with very small quantities of erbium.

Fraction VI.—The oxide was coloured an orange-brown. An intense absorption proved the presence of very much dysprosium, less holmium, and the merest possible trace of neodymium.

Fraction VII.—Reddish brown oxide. The absorption spectrum was very weak, showing the presence of a small amount of neodymium and traces of samarium and dysprosium. The green band of holmium could barely be detected.

Fraction VIII.—This gave an orange-brown oxide. The spectrum showed intense absorption bands, indicating the presence of a large quantity of neodymium, a very little praseodymium, and only a trace of samarium.

Fractionation of a mixture of earths, from monazite, giving more soluble double sulphates. The earths present consisted largely of gadolinium and dysprosium with small amounts of terbium, holmium, and neodymium.

The oxides were warmed with dimethyl phosphoric acid until entirely converted into dimethyl phosphates, after which the thick mass was stirred with water until dissolved.

The fractions were collected as follows:—Fractions I. to III. up to 95°; and fractions IV. and V. by evaporation of the mother-liquor from fraction III.

Fraction I. gave a brownish yellow oxide, which, when dissolved in nitric acid, gave a yellowish green solution. With the aid of the spectroscopic it was found that large amounts of dysprosium were present, accompanied by a little holmium.

Fraction II.—The oxide was chocolate-brown. Its nitrate solution was faintly green and showed weak absorption bands of dysprosium and terbium.

Fraction V.—Oxide red-brown. Absorption spectrum

indicated very small quantities of neodymium and dysprosium.

It will be observed from the above fractionations that the rate of separation of the rare earths is vastly greater than practically all the methods given up to the present time. Lanthanum, cerium, praseodymium, neodymium are left at once in the mother-liquor. Samarium, europium, and gadolinium are much less soluble than those previously mentioned, while they are more soluble than terbium, dysprosium, and holmium. Erbium, thulium, yttrium, ytterbium, &c., collect in the least soluble portions.

Since the solubilities of these compounds are the reverse of the usual type, they may be used for the rapid purification of many of the rare earths. For instance, we can easily remove traces of neodymium from samarium by this means, as the samarium dimethyl phosphate separates before the neodymium compound.

It is necessary to state that there is some inconvenience when working with the salts of dimethyl phosphoric acid, since they undergo gradual decomposition. A gelatinous precipitate is formed very slowly in the case of the rare earths, which filters with difficulty.

Durham, N.H.

REVIEW AND INTERPRETATION OF RECENT EXPERIMENTS WHICH EXTEND AND ELUCIDATE THE DOMAIN OF THE PASSIVITY OF METALS.*

By Dr. D. REICHINSTEIN, Zurich.

(Concluded from p. 4).

5. First Theory.

THE first theory was proposed at a time (1910-11) when the experiments of Le Blanc concerning the chemical polarisation of active metal electrodes were already known, and when the palladium-zinc experiments were made in order to clear the matter up; the other experiments mentioned above were not yet known, however. The theory, therefore, aimed at devising a mechanism which would admit of chemical polarisation without denying the possibility that a system, and a passive metal-anode likewise, might primarily emit anodic ions. I should like to emphasise at this place already that this question is more satisfactorily answered by this first theory than by the second one.

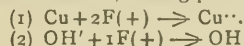
The first theory conceives a mechanism of the chemical polarisation after the type of the Pd-Zn electrode (Reichinstein, *Zeit. Elektrochem.*, 1911, xvii., 699). The rate of formation of the Pd-H alloy in the cathodic polarisation of the Pd-H₂SO₄ electrode is given by the momentary concentration of the Pd and H atoms near the boundary of the solid electrode and of the liquid electrolyte. Let us now assume that the contact with the electrolyte at the boundary electrode/electrolyte is not formed by the solid metal, but by a solution (=alloy) of all those substances whose ions are represented in the electrolyte. The volume which this hypothetical alloy occupies in the electrode is designated the *electrode volume*.

When we add to the electrolyte of the Pd-H₂-H₂SO₄ electrode some Zn salt, some zinc will be deposited in the electrode volume already at open circuit, because the thermodynamical equilibrium demands that the potentials H₂H⁺ ion and Zn-Zn⁺⁺ ion must finally be equal to one another.

We now make the assumption that the zinc entering the electrode volume diminishes the concentration of the Pd atoms there. When we now treat the electrode cathodically, the rate of formation of the Pd-H alloy will be smaller, and the polarisation will be greater,

than before. As a consequence some more zinc will be deposited on the electrode in accordance with the higher potential. The formation of the Pd-H alloy will proceed more slowly, and the polarisation will finally rise so high that zinc alone is deposited.

Analogously a Cu electrode has a certain oxygen concentration in the electrode volume already before the current is turned on. The potentials of the systems Cu-Cu⁺⁺ ions and OH⁻ ions always remain equal to one another, with or without the current flowing. That may be supposed to become possible by the splitting of the electric current into two components: two primary processes are *simultaneously* taking place at the anode—



Whilst the first process depresses the concentration of the Cu atoms in the electrode volume, the second process raises the O concentration there, and it is therefore the electric current which maintains the equilibrium in the electrode volume. Both the reactions increase the polarisation, and the purely chemical compensation processes oppose them. The process which is subject to chemical inertia is the oxidation of the massive copper by the aid of the oxygen in the electrode volume in the presence of the H⁺ ions of the electrolyte (any reaction between the oxygen of the electrode volume and the Cu atoms present in it is excluded, because there is equilibrium between the two systems, which, as we shall see, is a weak point of the first theory). When under special conditions the described oxidation takes place at a slow rate, the O concentration in the electrode volume and consequently the polarisation rise to a high degree, until finally another compensation process sets in, for example, O₂ generation (=passivity). The equations of this theory may be deduced as follows:—

Let there be: P₁, the electrolytic solution tension of the oxygen concentration in the alloy metal-oxygen, P₂ the electrolytic solution tension of its metal concentration, and $\hat{p}_1$ and $\hat{p}_2$ the corresponding concentrations of the ions in the electrolyte, which are assumed to be very high (=constant, practically not variable by small current densities). When the system tends to equilibrium, only P₁ and P₂ will change, and the conditions of equilibrium will be—

$$\frac{RT}{n_1 F} \ln \frac{P_1}{\hat{p}_1} + \frac{RT}{n_2 F} \ln \frac{P_2}{\hat{p}_2} = 0 \quad \dots (1)$$

or—

$$\sqrt[n_1]{\frac{P_1}{\hat{p}_1}} = \sqrt[n_2]{\frac{\hat{p}_2}{P_2}} \quad \dots (2)$$

In the most simple case where the chemical valencies n_1 and n_2 are equal we shall have—

$$P_1 P_2 = \hat{p}_1 \hat{p}_2 = K \quad \dots (3)$$

where K is a constant. When we bear in mind that according to our assumption there is always (current flowing or not) equilibrium between the systems oxygen-oxygen ions and metal-metal ions, we may interpret equation (3) to mean that, when the solution tension of the metal decreases as the current flows because its concentration in the alloy is reduced, the solution tension of the oxygen must decrease at the same time. We therefore write—

$$\delta P_1 \cdot P_2 = 0 \quad \dots (4)$$

By differentiating (4) we obtain—

$$\begin{aligned} \delta P_1 + \frac{\delta P_2}{P_2} &= 0 \\ -\frac{\delta P_1}{P_1} &= \frac{\delta P_2}{P_2} \quad \dots (5) \end{aligned}$$

If we now send the quantity of electricity r in the direction electrode-electrolyte, the system O OH⁻ will transport the fraction r of the quantity of electricity which will discharge OH⁻ ions and enrich the alloy in oxygen, whilst the electricity quantity $(1-r)$ will diminish the

* A Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, November 12, 1913. Translated from the German.)

metal concentration in the alloy. The relation between these two quantities is the following:—Let the potential of the alloy with regard to the electrolyte be π during a short interval, while the current is flowing. The work to be done in order to transport the quantity of electricity x from the electrode to the electrolyte will be—

$$\pi = r \frac{RT}{n_1 F} \ln \frac{P_1}{p_1} - (1-r) \frac{RT}{n_2 F} \ln \frac{P_2}{p_2} \quad (6)$$

The ratio of the increase in the oxygen concentration to the decrease in the metal concentration of the metal-oxygen alloy may be considered equal to the ratio of these two quantities of electricity; hence—

$$-\frac{\partial P_1}{\partial P_2} = \frac{r}{1-r} = \frac{P_1}{P_2} \quad (7)$$

and consequently—

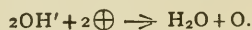
$$r = \frac{P_1}{P_1 + P_2} \quad (8)$$

By combining (8) with (3) we find—

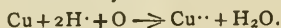
$$r = \frac{K}{K + P_2^2} \quad (9)$$

Or in words: *When with the anodic treatment of a metal its concentration in the metal-oxygen alloy becomes small, then the system O-OH' will effect the whole transport of electricity: r therefore becomes equal 1. The electrode now transports the electric current in a way, as if it were a highly noble metal; its capability of primarily forming ions is completely suppressed, and it is limited to a secondary formation of ions.*

Let us further assume that the total current in the anodic treatment of a copper electrode in the presence of H⁺ and of Cu⁺⁺ ions of high concentration be given by the reaction—



We will also suppose that the slow process of chemical compensation is defined by—



Let this process be much slower than the replenishing of the OH' ions which are consumed by the current. And finally let the experimental conditions be such that the rate of percentage rise in the Cu ion concentration at the electrode within the time t is so small that it may be neglected.

If, then—

x be the total oxygen concentration which the current has supplied up to the moment t ;

x_1 that concentration of the oxygen which has chemically been bound up to the moment t by Cu and H' ions;

$c = x - x_1$ the oxygen concentration on the electrode surface at the moment t ;

k_0 the velocity coefficient of the reaction:



i a variable current intensity for which the same direction is, however, always maintained;

and if, as stated, the oxygen concentration on the electrode surface at the moment t be—

$$c = x - x_1. \quad (10)$$

then the concentration at the moment $(t+dt)$ will be—

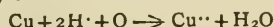
$$c + dc = x + dx - (x_1 + dx_1) \quad (11)$$

According to Faraday's law

$$dx = ki(t)dt \quad (12)$$

where k is a proportionality factor.

The velocity of the reaction —



$\left(\frac{dx_1}{dt}\right)$ is at any moment proportional only to the actual oxygen concentration because the concentration of the

metallic copper is *eo ipso* constant, and the concentration of the H' ions constant by hypothesis, and we obtain finally—

$$dc = (ki(t) - k_0 c)dt \quad (13)$$

from which we find—

$$c = e^{-k_0 t} \left(C_1 + \int_0^t k i(t) dt \right) \quad (14)$$

where C_1 is the integration constant. From the initial condition (for which $t=0$) we see at once that the integration constant is dependent only upon that oxygen concentration which corresponds to the electrode when no current is flowing. This value of c is in our case given by the equilibrium potential of the copper electrode. If we now consider that the chemical polarisation of a type of electrode such as we deal with in the copper electrode will, at small current density already, assume relatively large values, which differ strongly from the equilibrium potential of the base electrode, C_1 may be regarded as infinitely small with respect to the c values, and the equation may be written in the form—

$$c = k e^{-k_0 t} \int_0^t i(t) dt \quad (15)$$

This theory, which very satisfactorily characterises the chemical polarisation on condition that all the metals become primarily active as anodes, fails in many instances. Without entering into detail I will emphasise the consideration which will help us on to the right way.

We have seen that in the consideration of the anodic treatment of a metal the theory leads to quasi-secondary formation of ions, although in principle the theory starts from primary anodic formation of ions. That is just the desired result of the theory. This result is not arrived at, however, when we attempt to explain the cathodic chemical polarisation by the aid of this theory. For if we imagine that the two chief components of the electrode volume consist, in the cathodic polarisation of the Cu-CuSO₄ electrode, of Cu and of H atoms, then their quotient is constant, not their product, and the increase in the concentration of the one calls forth a simultaneous increase in the concentration of the other.

Further—and that is the chief drawback of the theory—we cannot, with its aid, come to the above-mentioned type of two reactions, of which the one is retarded by a rise in the O concentration whilst the second increases its velocity in a regular manner. This type of two reactions, we have recognised, can alone elucidate the phenomena of passivity. We can easily comprehend that we shall arrive at such a type of reaction if we imagine some reaction to take place within the electrode volume, *i.e.*, between its constituents. The first theory does not admit of that, because there is always equilibrium within the electrode volume; and all the compensation processes of which the first theory admits are indirect reactions. In order, therefore, that we may imagine a larger number of possible compensation processes, the mechanism of the electrode volume should be so designed that there should not prevail equilibrium in it while the current is flowing. The entire current must be transported by *one* system from the electrode to the electrolyte.

We also saw that the prototype of the mechanism of chemical polarisation, the Pd-Zn experiment, renders it necessary to ascribe to the zinc which enters the electrode volume a diminution of the concentration of the Pd atoms. How is this to happen? This effect is difficult to conceive if we regard the electrode volume as constant, and if we make no new hypothesis as to the mutual influences of the various constituents of the electrode volume. The simplest assumption which at once enables us to describe all the experiments mentioned is this: *The sum of the concentrations of all the constituents of the electrode volume is always constant, whether the current flows or not.*

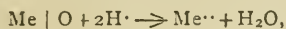
6. The Constant-Sum Hypothesis and the Second Theory.

(Reichenstein, *Zeit. Elektrochem.*, 1913, xix., 672).

We presume that the electrode volume is always fully saturated, and that any new constituent, possibly introduced by the electric current, ejects part of the old substances.

For the present I am not in a position to maintain the idea of a primary activity of all the systems. In view, however, of the fact that this theory satisfactorily answers all the questions concerning the chemical polarisation, as well as those concerning the spontaneous solution of solid bodies in the presence of oxidising agents, we may for the present rest satisfied with the assumption that in aqueous solutions the transport of the electric current across the boundary electrode/electrolyte is effected only by the OH' and the H' ions.

When a metal electrode is treated anodically the oxygen introduced pushes the metal atoms out of the electrode volume—the same will happen on the cathode by the H₂ introduced—and the chemical equilibrium prevailing before the current was flowing will be destroyed. The oxygen now begins to react with the metal atoms of the electrode volume. Let this reaction be of the form—



where Me and O are respectively an atom of the metal and of the oxygen of the hypothetical alloy, and H' concerns the electrolyte.

If the concentrations of the three substances reacting with one another are x, y, z , the velocity of the compensation process can be formulated as follows:—

According to the hypothesis of the constant sum

$$x + y = a \quad \dots \dots \dots (16)$$

where a is a constant; the velocity v

$$v = k_0 z^x x y = k_0 z^x y (a - y) \quad \dots \dots (17)$$

when, in a special case, z is a constant, the $(v - y)$ curve has a maximum. Now—

$$v = k'(ay - y^2) \quad \dots \dots \dots (18)$$

from which

$$\frac{dv}{dy} = ak' - 2k'y$$

and

$$\frac{d^2v}{dy^2} = -2k'.$$

The maximum corresponds to the value $y = \frac{a}{2}$.

When with a certain current density of the electrolysis the compensation process is so rapid that the oxygen concentration of the electrode volume does not rise above the value $\frac{a}{2}$ (which we may call the *critical concentration*),

then there will be no reason to fear that another compensation process will set in, e.g., generation of oxygen (=passivity). When, however, the critical concentration is exceeded, the compensation process will necessarily be retarded, and the O concentration will increase rapidly until a new compensation process sets in. Instead of the above-mentioned equation of the first theory, which defines the accumulation of the O concentration in the electrode volume after closing the circuit:—

$$\frac{dy}{dt} = ki - k_0y,$$

where i is the current intensity of the continuous current, we have now—

$$\frac{dy}{dt} = ki - v \quad \dots \dots \dots (19)$$

and by combining (19) and (18)—

$$\frac{dy}{dt} = ki - k'ay + k'y^2 \quad \dots \dots \dots (20)$$

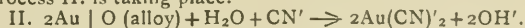
This equation gives us the above-discussed point of inflection for the $y-t$ curve, that is to say, also for the curve which illustrates the rise of the polarisation with time after closing the circuit.

We have now arrived at some point of reference enabling us to describe the experiments of Andrejew.

When we immerse a foil of gold in a solution of KCN which contains an oxidising agent like O₂, H₂O₂, or O₃ in solution, two purely chemical reactions will come into play:—

I. The formation of the gold-oxygen alloy.

This process is missing in the electrolytic dissolution of metals because in their instance the oxygen is directly supplied by the primary discharge of OH' ions, whilst here the oxygen is supplied by a chemical reaction (= decomposition of the oxidising agent). If the oxygen were not to disappear owing to the dissolution of the gold, we should finally arrive at an equilibrium between its concentration in the electrode volume and the concentration of the oxidising agent in the aqueous KCN solution. We may suppose that in one and the same oxidising agent these two concentrations will bear a rectilinear relation. Now the formation of the gold-oxygen alloy, we shall see, does not proceed at an infinitely rapid rate, yet not so slowly that this process should become decisive for the entire process of solving the gold. The CN' ions are, moreover, not in contact now with the compact gold metal, but in contact with the gold-oxygen alloy, and process II. is taking place.



This process may, of course, proceed in several stages. When we increase the O concentration of the alloy by increasing the concentration of the oxidising agent in the liquid phase, the critical O concentration will finally be exceeded, and the velocity of the process II. will diminish more and more.

It should here be emphasised that there are many instances in which the rate of oxidation becomes smaller as the oxygen concentration is raised; I will content myself with drawing attention to the table of these cases compiled by van't Hoff ("Vorlesungen über theoretische und physikalische Chemie," No. 1, Braunschweig, 1898, 238).

The critical O concentration has now been exceeded, and, in accordance with what has been explained, a new chemical process (a second compensation process) must come into play. Such processes are the following: formation of H₂O₂ (observed by Bodländer), formation of gold peroxide.

We recognise that the occurrence of oxide layers must not be regarded as the cause of the delay in the solution of gold. The peroxide films are merely a concomitant feature, which indeed indicates that the O concentration of the alloy has attained high values, but which must by no means be represented as the cause of the dissolution of gold. It is a symptom, like the rise of temperature in the diseased human body.

It is interesting to note that some investigators regard as cause of the passivity that in which other investigators see the consequence of the cause of passivity.

Thus, process I. supplies oxygen to the alloy metal-oxygen, and temporarily increases its concentration, whilst process II. tends to diminish this concentration. In the stationary condition, when the reactions proceed at a constant rate, the concentration of the oxygen in the alloy is dependent upon the two processes I. and II.; that is to say, the O concentration may be increased, not only by increasing the rate of process I., but also by diminishing the rate of process II. *Ceteris paribus*, therefore, the "critical O concentration" (in the process of dissolving gold in diluted KCN) may be exceeded with the aid of oxidation potentials of the oxidising agents, which are so low that they would be ineffective at higher CN' ion concentration. This is in agreement with the experiments of Andrejew, according to which the characteristic film of gold peroxide appears in solutions of KCN ranging from 0.01 to 0.05 per cent, already when air acts as oxidising

agent, which demonstrates that process I. is absolutely necessary. We may draw a comparison as to the spontaneous solution of passive and of active metals in the presence of oxidising agents from this point of view. What could we predict as regards the spontaneous solution of copper and nickel in H_2SO_4 in the presence of oxidising agents? We know that the latter of these two metals belongs to the so-called passive metals, *i.e.*, that the process of solution is slow. We should then expect, from what has been explained, that the critical O concentration of the nickel-oxygen alloy, and hence the retardation in the rate of solution of nickel, will, *ceteris paribus*, always occur at such oxidation potentials of the oxidising agent at which this will not be attainable in the case of copper; and it is altogether doubtful whether the v maximum will experimentally be realised in the dissolution of copper.

Of especial interest from the standpoint of the new theory are the exposition of the cases of the palladium-zinc cathode and the behaviour of the alloys mentioned on the anode.

When a palladium electrode, to the electrolyte of which a zinc salt has been added, is treated cathodically, the current is carried by the H ions. Owing to the prevailing conditions of equilibrium, some zinc will enter the electrode volume and will push out some palladium, already before the circuit is established. When the current flows, the zinc acts as ballast, because it depresses the Pd concentration according to the hypothesis of the constant sum, and hence retards the rate of the compensation process. When the concentration of the zinc in the electrode volume is γ and the sum-constant is a , the maximum of the curve, which expresses the rate of the compensation process (Pd + H reaction) as a function of the H concentration, will correspond, not to the H value, $\frac{a}{2}$, but to

$\frac{a - \gamma}{2}$. Now, hydrogen accumulates more and more in the

electrode volume, and the polarisation rises. It should be noted that the whole conception forces us to assume a chemical reaction between the H atoms and those Pd atoms which fill up the electrode volume—an assumption which was impossible according to the first theory of there being always equilibrium in the electrode volume. Thus quite generally any foreign substance entering into the electrode volume which will not take part in the compensation process may be regarded as ballast.

A special interest attaches, from this point of view, to the behaviour of the real alloys forming on the anode. When, in the case of a purely active metal, the maximum of the curve O concentration/velocity cannot be attained, that maximum can, in the case of an alloy as described, be realised, owing to the ballast, at relatively low current density, and the curve will show an inflection. An alloyed anode, therefore, displays formally the properties of a passive metal. We may imagine the whole anodic process on the following lines. As regards the space distribution the electrode, at the beginning of the anodic treatment, has the appearance: *Electrolyte/hypothetical alloy/real alloy/compact base metal*. The anodic treatment carries oxygen into the hypothetical alloy, where it partly displaces both the metals, and the chemical reaction between the oxygen and the base metal sets in. (As a matter of fact the two metals enter into competition with regard to the oxygen; practically, however, the oxygen reacts with the less noble metal only.) The base metal, which has disappeared owing to the chemical reaction, is being replaced in the hypothetical alloy by both the metals of the real alloy. In which ratio? That depends upon the rate of diffusion of the base metal, or upon the rate of the alloy formation of the two metals. If this rate be small, then the concentration of the base metals in the hypothetical alloy (when the current is flowing) will also be small—the velocity of the compensation process will decrease, the polarisation will rise, and finally will follow the decomposition of the real alloy; the electrode then

will have the following spatial distribution: *Electrolyte/hypothetical alloy/thin layer of the noble metal/compact base metal*. The noble metal may then separate from the electrode. For this end, we know from galvanoplastic processes, a trace of impurity between the two metals will be sufficient.

In order to keep the rate of alloy formation alluded to small, we must, as has been pointed out already, exercise the greatest care as to the purity of the two metals in building up the real alloy. Certain foreign substances accelerate the alloy formation; nitric acid in particular should here be mentioned; it plays the part of the soldering liquid in soldering two metals.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

THE REDDENING OF LEAVES.

Prof. Gaston Bonnier has presented to the Academy of Sciences a new study of M. Raoul Combes, concerning the crystallisable substances that are found in leaves. One of these substances of a yellow colour is found in green leaves; it is this substance which produces the reddening of leaves in autumn. M. Combes, who had obtained outside the organism the synthesis of the red substance, by starting from the yellow substance by reduction, has just obtained the inverse, that is to say, the synthetic production of the yellow substance, by starting from the red substance, by oxidation. Thus the general question, the answer to which has been so long sought after in vegetable physiology, has at last been solved. Besides its general importance in the life of plants it is easily understood that this solution may be susceptible of practicable applications, notably in what concerns the different varieties of vines.

THE ORIGIN OF PETROLEUM.

Learned men are not agreed as to the origin of petroleum. Two schools exist; one of which attributes the formation of petroleum to the igneous action of carbides on water; the other school considers that the petroleum proceeds from a distillation of vegetable origin. Prof. Armand Gautier, following on the recent studies of MM. Aimé Pictet and Maurice Bouvier, which he has made known to the Academy of Sciences, gives the preference to the second hypothesis of a vegetable formation. The two learned Geneva gentlemen have distilled ordinary coal at a pretty low temperature, somewhere about 450° in vacuum. They have thus obtained a special kind of tar vacuum, tar without any phenol or any aromatic hydro-carbides. Washed with alkali and sulphuric acid this vacuum tar treated by sodium gives a powdery product having a discharge of hydrogen. This body dissolved in water gives birth to semi-aromatic alcohols, derived from camphor and from hydrocarbides, having the formula $\text{C}_{10}\text{H}_{20}$ or $\text{C}_{12}\text{H}_{22}$, which have the same characteristics as the Canadian petroleum, the same point of fusion, same smell, &c. These are quite new experiments and of the greatest interest.

THE SPRING FINDERS.

At the time of the famous experiments undertaken at the second Congress of experimental psychology by the spring finders and adepts of the divining rod, M. Armand Viré, Professor at the Natural History Museum, was exceedingly incredulous. However, he became converted, and indeed became a spring finder himself, and, as it were, in spite of himself. And it must be admitted that his conversion caused some astonishment. During the summer months he invited several spring finders to the grottoes of Padriac, with which he is specially well acquainted and of which the plans have not been published. There were several negative experiments. But two or three spring finders were remarkably successful. On the surface of the soil they followed several subterranean water springs and

arrived at the points where they left the earth and appeared on the surface. These points were previously unknown by the spring finders. M. Edmond Perrier, when presenting these experiments to the Academy of Sciences, added that neither he nor M. Armand Viré take upon themselves the responsibility of these observations. They offer no explanations, but simply give the mere facts.

THE MAP OF THE WORLD TO A SCALE OF ONE MILLIONTH.

M. Charles Lallemand, Director of the Service and Organisation of the General Levelling of France, has given some information concerning the last conference of the international map of a millionth scale. At the first conference, which was held at London in 1909, only seventeen countries were represented. At the present time thirty-one states have joined the convention. M. Lallemand also announced that the Prince of Monaco was taking upon himself the expense of several oceanic pages.

MICROBIAN LIFE.

Microbian cultures are often very difficult. M. Adrien Lucet, Member of the Academy of Medicine, has just shown that a regular agitation or shaking of the liquid mediums used in bacteriology, contrary to the opinion that is generally admitted, acts favourably on these infinitely little creatures. By making these bouillons undergo a slow and continuous movement he has, in fact, been able to obtain cultures as many as eight times more abundant of the microbes of cholera, typhus fever, carbuncle, diphtheria, the glanders, dysentery, and even of lock-jaw, the microbe of which can only be cultivated without the penetration of any air. It was M. Chauveau who communicated M. Lucet's study to the Academy.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 20th, 1913.

Prof. W. H. PERKIN, LL.D., F.R.S., President,
in the Chair.

MESSRS. R. E. Slade and S. C. Sastry were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Albert Frederick Calvert Royston, Eton Avenue, N.W.; Behari Lal Das, 107/2/1, Manaharpukur Road, Kalighah, Calcutta; Eric Russell Harrap, Maisemore, Ebury Road, Rickmansworth, Herts; Oswald Ryle Horwood, M.A., M.R.C.S., L.R.C.P., Tunstall Rectory, Suffolk; Dan Ivor James, M.A., B.Sc., Frondeg, Llandilo, Carmarthenshire; Alexander Williamson McLaren, 3, Hayfield Terrace, Langside, Glasgow; Harold Edwin Temple, 239, Cashel Street, Christchurch, New Zealand; Robert James Wright, M.A., care of R. Burnett, Esq., 336, Pollokshaws Road, Glasgow.

A Certificate has been authorised by the Council for presentation to ballot under By-law I.(3) in favour of Mr. Bertie Mandel Welsh, 80, Hunter Street, Sydney, N.S.W.

The PRESIDENT announced:—I. That the bust of the Rt. Hon. Sir Henry Roscoe which was exhibited at the meeting had been presented to the Society by the friends and former students of Sir Henry Roscoe.

2. That by request of the Council Messrs. Vieweg and Sohn have offered to sell the first volume of the "Literatur Register," by R. Stelzner, to Fellows of the Chemical Society at the reduced price of £3 10s. (original price £4 4s.), provided that not less than twenty copies are sold to Fellows of the Society. Those Fellows who desire to obtain a copy of the "Literatur Register" on these terms are requested to send in their names to the Honorary Secretaries.

The PRESIDENT referred to the meeting of the International Association of Chemical Societies which had been held in Brussels during September, 1913, and drew the attention of Fellows to the abbreviated report of the meeting which the Council have ordered to be printed in the *Proceedings*.

Of the following papers, those marked * were read:—

*286. "Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part V. The Simpler Esters of the Carbinols, $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{R}$." By ROBERT HOWSON PICKARD and JOSEPH KENYON.

The following homologous series of esters of normal aliphatic acids have been prepared and examined polarimetrically under various conditions:—(i.) The esters of *d*-methyl-ethylcarbinol; (ii.) the esters of *d*-methyl-*n*-propylcarbinol; (iii.) the esters of *d*-methyl-*n*-butylcarbinol (iv.) the esters of *d*-methyl-*n*-amylcarbinol; (v.) the esters of *d*-methyl-*n*-hexylcarbinol; (vi.) the esters of *d*-methyl-*n*-nonylcarbinol [these six series range from the acetates to the stearates]; (vii.) the acetates and (viii.) the *n*-dodecoates of the *d*-carbinols [methylethylcarbinol to methyl-*n*-undecylcarbinol].

Many of these esters (all of very simple constitution) exhibit anomalous dispersion when examined polarimetrically at temperatures above 150° or at various concentrations in solvents such as pyridine, benzene, or carbon disulphide.

*287. "Co ordination of Rotatory Powers for different Wave-lengths, Temperatures, and Solutions." (Preliminary Note). By ROBERT HOWSON PICKARD and JOSEPH KENYON.

The authors have already described the synthesis of thirty optically active carbinols of the general formula $\text{R}\cdot\text{CH}(\text{OH})\cdot\text{R}^2$, and some seventy esters derived from some of them. These compounds have been examined polarimetrically for three wave lengths (a) in the homogeneous state at different temperatures, and (b) in several solvents at various concentrations. It was found (see preceding paper) that many of these under certain conditions exhibited anomalous optically rotatory dispersion.

The attention of the present authors was therefore directed to a paper by H. E. Armstrong and E. E. Walker entitled "The Causes of Variation in the Optical Rotatory Power of Organic Compounds and of Anomalous Rotatory Dispersive Power" (*Proc. Roy. Soc.*, 1913, A, lxxxviii., 388). In this paper it is suggested that anomalous dispersion is caused by the presence of two substances (in the actual cases considered of two isodynamic forms) having rotatory powers of opposite sign and different dispersive powers.

In the case of esters of such simple constitution as those described in the preceding paper, the suggested explanation of the anomalous dispersion seems feasible, however, only on the assumption of a change in the association of the esters, not only in the homogeneous state on increase of temperature, but also on solution in various solvents.

A "characteristic diagram" for *d* sec.-octyl acetate was therefore constructed according to the method of Armstrong and Walker (*loc. cit.*). A reference line with slope of unity was drawn, and on it were plotted the various numbers representing the specific rotatory powers for mercury-green light. The numbers representing the specific rotatory powers for sodium-yellow and mercury-violet lights were then plotted on the ordinates passing through the points previously located on the reference line. The various points for the latter two lights were found to lie on two straight lines, and the diagram was similar in character to those for the substances of previously known anomalous dispersive power as drawn and described by Armstrong and Walker.

It is now found, however, that this same "characteristic diagram" can be used to co ordinate the results of all the determinations of rotatory power of one of the two optically active forms of the hundred synthetical com-

pounds previously described by the present authors; thus the numerical results (varying from +50 to -25) of the determinations of rotatory power for the three lights in different solvents at all concentrations and in the homogeneous state at different temperatures, not only of one compound, but of many (all of which are of very simple, but closely related constitution), have been plotted on one diagram. In this the various values lie on three straight lines, which intersect above the zero-line, and not all at one point. The dispersions then appear in the diagram as some function varying with the magnitude of the rotatory powers, thus co-ordinating the small, but very definite, differences in the dispersions of the homologous compounds which have been observed experimentally.

It cannot yet be said whether this co-ordination is due either (i.) to the comparison of a large number of compounds which have very similar dispersive powers, or (ii.) to the closely related constitutions of the substances.

This method of plotting appears to afford (in some cases at least) a means by which a derivative differing in sign from that of the optically active parent substance can be properly designated "d" or "l," and also a means of determining whether a change in configuration has taken place in the formation of a derivative.

DISCUSSION.

Sir W. RAMSAY suggested that the cause of rotation was ultimately in the direction of the circular motion of electrons within the molecule. A dextrorotatory substance, say, might have hydroxy in the molecule, capable of repelling an electron, and causing it to rotate dextrorotatorily. On the other hand, if the hydroxyl be replaced by bromine, the bromine atom might have the property of attracting an electron and of reversing the direction of its rotation. This suggestion was made, not with any conviction of its applicability, but merely for consideration as to whether it was possible to obtain any clue to the fundamental reason of rotation.

*288. "The Interaction of Sodium Amalgam and Water." By HERBERT BRERETON BAKER and LESLIE HENRY PARKER.

Water distilled under special conditions has a visibly slower rate of action on sodium amalgam than ordinary distilled water. An apparatus was constructed to measure accurately the hydrogen evolved, and various samples of water were tested. The least active specimens of water were obtained by distillation from copper or platinum apparatus, especially on superheating the steam before the latter was condensed.

The rate of action was shown to be no function of the conductivity of the water used, but was found to depend largely on the pressure at which the reaction was conducted, increase of pressure causing the rate of action to diminish, and *vice versa*. Various explanations of this phenomenon were put forward and tested, but the only feasible one was the assumption of the presence of some impurity in minute quantity, which was volatile under the conditions of ordinary distillation, but was destroyed on heating to redness. Experimental evidence was adduced which seemed to show that the only impurity which satisfied all the conditions was hydrogen peroxide, and the widely differing activities of various samples of water on sodium amalgam is ascribed to the presence of varying quantities of hydrogen peroxide.

*289. "The Action of variously treated Waters on Sodium Amalgam." By LESLIE HENRY PARKER.

Further evidence was adduced in support of the explanation of the varying activity of different samples of water on sodium amalgam put forward by Baker and Parker (preceding paper).

Various metals were sealed up with a quantity of the inactive water for definite periods. Metals such as copper, mercury, &c., did not have much effect, whilst aluminium increased the activity of the water on sodium amalgam. This was shown to be in harmony with Traube's work on the wet oxidation of metals (*Ber.*,

1882, xv., 670). Exposure to radium bromide also increased the activity. This is in accordance with the work of Kailan (*Monatsh.*, 1912, xxxiii., 1329).

DISCUSSION.

Dr. SENTER suggested that the results would probably come under the heading of over-voltage phenomena, the best-known example of which was the retarded action between pure zinc and sulphuric acid. Over-voltage at the boundary between solid and liquid appeared to be connected with surface tension, and it might be assumed that the active substance, whatever it might be, modified the surface tension.

With reference to the author's proof of the presence of hydrogen peroxide in tap water, tests depending on the liberation of iodine from iodides were rather untrustworthy, as in certain circumstances dissolved oxygen gave the reaction in question. The titanium dioxide test was trustworthy, and was extremely sensitive, as it was capable of detecting 1 part of peroxide in 50 million parts of water (compare Senter, *Trans. Faraday Soc.*, 1906, ii., 142), and the fact that it was not given by the water in question appeared to render further investigation desirable. The effect of added hydrogen peroxide might be connected with the fact that this compound was readily decomposed at a mercury surface (Bredig); the evolution of oxygen would presumably disturb the very unstable equilibrium characteristic of over-voltage.

Dr. R. E. SLADE agreed that it was to be expected that hydrogen peroxide would disturb the over-voltage at the surface of the amalgam in the manner suggested by Dr. Senter. He believed, however, that a very important factor was the existence of dust particles in the water, and quoted the work of G. N. Lewis on the potential of sodium amalgams in support of this. The experiment which Mr. Parker has just shown rather pointed to this theory, for in the tube of pure water the bubbles of hydrogen came off at a few points which moved about on the surface of the amalgam. Perhaps the superheating of the steam was an efficient way of removing particles of dust by destroying them or by causing them to adhere to the hot tube.

Dr. KEANE asked whether the influence of light had been studied in connexion with the experiments described, as this might have considerable effect both in regard to the production and decomposition of hydrogen peroxide.

In reply to Dr. Senter, Mr. PARKER said that no comparative experiments had been made as to the relative values of the tests for hydrogen peroxide: further experiments were in progress with the view of obtaining some light on the mechanism of the reaction. In reply to Dr. Keane, he also stated that no experiments had been tried on the influence of light on the reaction.

*290. "The Polymerisation of Cyanamide." By GEORGE FRANCIS MORRELL and PETER BURGEN.

The polymerisation of cyanamide, under various conditions, both in the solid state and in solution, and also under the influence of catalysts, has been quantitatively studied. With the pure substance itself only about 10 per cent was found to have changed in six months, and in aqueous solution, even at elevated temperatures, the reaction proceeds comparatively slowly, many hours' heating at 100° being required to complete it. In absolute alcoholic solution the reaction-velocity is much further reduced. In all these cases the velocity-constant was not that of a bimolecular reaction, but equal amounts were found to be changed in equal intervals, except at great dilution, in which case a logarithmic curve was obtained. An ionic explanation may be advanced to explain these facts, the ions present in very small and, at first, practically constant concentration alone taking part in the change. The influence of acids and bases, such as sulphuric acid, ammonia, and sodium hydroxide, as catalysts produces an extremely marked acceleration, very small quantities reducing the period of half-change in aqueous solution at 100° from about twelve hours to as many

minutes. Increasing quantities of sodium hydroxide produced increasing acceleration up to a point corresponding with the addition of 0.25 equivalent, but the further addition brought about a slight retardation, so that a solution containing sodium cyanamide, although it polymerised much more rapidly than pure cyanamide (half period at 100°, thirty minutes, compared with twelve hours in the latter case), yet did not do so more quickly than one containing less than 1/30th of the amount of hydroxide. The velocity-constant of these reactions was found to be between that of a unimolecular and of a bimolecular reaction, which latter stage it would only reach, on the authors' hypothesis, at infinite dilution and complete ionisation.

DISCUSSION.

Dr. MORRELL, in reply to Dr. Forster, stated that the method found most satisfactory for isolating cyanamide from its sodium salt was to neutralise a well-cooled concentrated aqueous solution of the latter with oxalic acid. The precipitated sodium oxalate was filtered off, and the filtrate evaporated almost to dryness in a vacuum. From this residue the cyanamide was extracted with ether, in which other substances present were insoluble. It was finally purified by recrystallisation from the same solvent.

*291. "Some Derivatives of Oleanol." By FRANK TUTIN and WILLIAM JOHNSON SMITH NAUNTON.

Oleanol, $C_{31}H_{50}O_3$, a crystalline substance from olive leaves (Power and Tutin, *Trans.*, 1908, xciii., 896), has been further investigated. On oxidation with potassium permanganate it yields oleanone, $C_{29}H_{44}O_2(OH)_2$, which gives a mono- and di-acetyl derivative.

Oleanone, when heated with dilute acetic acid, undergoes a profound change, the reaction products containing a substance, $C_{50}H_{76}O_7(OH)_2$. An analogous change occurs when diacetyloleanone is heated with a mixture of acetic and hydrochloric acids. The monoacetyl derivative, $C_{50}H_{76}O_8(OH)_2 \cdot CO \cdot CH_3$, thus produced, on hydrolysis with alkali, yields the above-mentioned dihydroxy-compound.

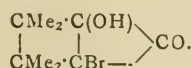
On oxidation with chromic acid, oleanone yields a substance, $C_{29}H_{41}O_3 \cdot OH$ (m. p. 275°), which, when heated for two hours with alcoholic alkali, gives an isomeride, melting at 315°. Both substances yield monoacetyl derivatives.

When oleanol itself is oxidised with chromic acid the above-mentioned substance, $C_{29}H_{42}O_4$ (m. p. 275°), is formed, together with a mixture of at least three carboxylic acids.

292. "Some Derivatives of Phorone." Part I. By FRANCIS FRANCIS and FRANCIS GEORGE WILLSON.

An investigation of some derivatives of phorone has been commenced by the study of a phorone dibromide obtained from the tetrabromide by the action of pyridine.

The most characteristic reaction of this dibromide is the ease with which it is converted by concentrated sulphuric acid into a crystalline derivative, a study of the oxidation and reduction products of which has led to the conclusion that it is 4-bromo-2:2:3:3-tetramethylbicyclo [0, 1, 2]pentan-1-ol-5-one,



The oxidation and reduction products were described; among the former is tetramethylsuccinic acid, and among the latter 1:1:2:2-tetramethylcyclopentan-4-one, a substance with properties curiously similar to those of camphor.

The derivative also gives rise on bromination to a dibromide possessing characteristic properties.

293. "The Porosity of Iron." By WILLIAM HUGHES PERKINS.

An attempt has been made to correct or confirm the

conclusion of Friend that iron is slightly porous (*Trans.*, 1912, ci., 50). It is concluded that only very small quantities of the alkalis, and therefore presumably of other salts, are retained under prolonged washing. The quantity of ammonia retained by iron after about fifteen to twenty minutes' washing is probably not more than about 0.0000001 gm. per sq. cm.

294. "The Bleaching Action of Hypochlorite Solutions." By SYDNEY HERBERT HIGGINS.

Bleaching powder solution to which an excess of boric acid has been added has very energetic bleaching properties because the boric acid merely liberates hypochlorous acid from the hypochlorite, whereas an excess of hydrochloric acid produces free chlorine and a solution of very weak bleaching properties. If, however, calcium carbonate is added to the latter solution, hypochlorous acid is regenerated, and the bleaching properties are restored. The addition of hydroxides to hypochlorite solutions opposes the hydrolysis of the hypochlorite, and retards the bleaching action, whereas the addition of small quantities of acids assists the hydrolysis and stimulates the bleaching action; the effect on the bleaching properties of the solution is due to the active mass of the free hypochlorous acid present, being in the one case reduced and in the other augmented. Even in the presence of a large excess of hydroxides the solutions have a small bleaching effect, which is probably due to a small amount of hypochlorous acid being still present in solution in spite of the opposition of the hydroxide to the hydrolysis of the metallic hypochlorite. All the experiments point to the conclusion that hypochlorite solutions entirely owe their bleaching properties to the free hypochlorous acid present in solution. Sometimes there is a secondary reaction between the hypochlorous acid and any neutral chloride present, producing nascent chlorine of energetic bleaching properties (*Proc.*, 1912, xxviii., 130), but the main action is one of direct oxidation by the hypochlorous acid. During the bleaching action chlorides are produced by the reduction of the hypochlorites, but the stimulating effect of chlorides thus produced on the bleaching action is negligible.

295. "Guaiaicum Resin as a Reagent for the Detection of Oxydases and of Minute Traces of Copper." By WILLIAM RINGROSE GELSTON ATKINS.

In order to ascertain how far traces of metals might vitiate tests for oxydases by guaiaicum resin, a series of experiments was carried out to determine the limits of sensitiveness of the reaction towards certain salts. Adopting the methods usual in water analysis, it was found that very minute amounts of copper salts or of potassium permanganate may be detected by this test. Accordingly it is brought forward as a reaction of utility in water analysis. Below are recorded the limits of sensitiveness of the reaction, expressed in gms. per cc. Copper as sulphate, 2×10^{-9} to 2×10^{-8} . Potassium permanganate, 4×10^{-6} . Potassium dichromate, 1×10^{-7} . Iron, as ferrous sulphate, 1×10^{-6} , as ferric sulphate, 1×10^{-6} . Lead as acetate, 6×10^{-6} . Nitric acid, 2×10^{-5} . Manganese as sulphate, 8×10^{-4} . In each case a few drops of hydrogen peroxide were added, as well as a very dilute solution of the reagent. Traces of chlorides were also present, and play an important part.

296. "The Absorption Spectra of various Derivatives of Pyridine, Piperidine, and Piperazine in Solution and as Vapours." By JOHN EDWARD PURVIS.

The absorption spectra of a number of the derivatives of pyridine, piperidine, and piperazine, both in solution and in the vaporous condition, have been investigated. The general results show that, besides the nature of the molecule, the type, the number, and the orientation of the side-chains influence the production of the narrow vapour bands; and that, when these bands disappear, the remaining bands are generally comparable with the solution bands.

297. "Derivatives of *p*-Iodoaniline." By FREDERICK DANIEL CHATTAWAY and ALFRED BERTIE CONSTABLE.

The ease with which chlorine and bromine substitute arylamines has led to a very complete knowledge of the simpler derivatives which they form, but comparatively few of the corresponding iodine compounds have been prepared on account of the difficulty of effecting iodine substitution and the readiness with which the iodoanilines decompose.

The conditions necessary to obtain a good yield of *p*-iodoacetanilide, and from it to prepare *p*-iodoaniline, were described. The aniline having been obtained in quantity, a number of its simpler derivatives have been prepared.

298. "The Interaction of Tetranitromethane and Compounds containing Centres of Residual Affinity." (Preliminary Note). By ERNEST MAGOWAN HARPER and ALEXANDER KILLEN MACBETH.

The work was undertaken to investigate the colours developed on adding tetranitromethane to various substances. Ostromisslensky (*Journ. Prakt. Chem.*, 1911, [2], lxxxiv., 349) has recorded such effects with aromatic amines, and also with aliphatic compounds containing the ethylenic double linking. Clarke, Macbeth, and Stewart (*Proc. Chem. Soc.*, xxix., 161) have shown that these are only particular cases of a more general phenomenon. Colours have been obtained with organic sulphides, iodides, phosphines, amino-compounds, &c.

The method employed was to photograph tetranitromethane in an alcoholic solution of the substance of constant strength. Tetranitromethane itself gives no colour in dry alcohol. With the sulphides a yellow colour is produced on mixing the solutions, but the absorption spectrum does not differ greatly from that of tetranitromethane. The colour deepens on keeping, and after some time the spectrum undergoes a great change. A band is developed in the region $1/\lambda$ 2800—2900; thus tetranitromethane with *N*/10-pentamethylene sulphide after fourteen hours shows a band the head of which is at $1/\lambda$ 2850 in the log-thickness 35 of *N*/100,000-solution.

With compounds containing an ethylenic double bond a similar band is obtained; thus tetranitromethane with *N*/10-amylenes after five days gives a band the head of which is at $1/\lambda$ 2850 in the log-thickness 32 *N*/100,000-solution.

Similar bands are obtained with sulphur compounds other than the sulphides (ethyl mercaptan, &c.), and with various aliphatic amino-compounds, the band development being exceptionally rapid in these cases.

In most cases the penetration of the band increases with time, thus:—

	Band head.	Log-thickness <i>N</i> /100,000.	Time. Days.
<i>N</i> /10-amylenes	$1/\lambda$ 2850	32	5
<i>N</i> /10-amylenes	$1/\lambda$ 2850	26	10
<i>N</i> /10-pentamethylene sulphide	$1/\lambda$ 2850	33	2
<i>N</i> /10-pentamethylene sulphide	$1/\lambda$ 2850	28	5

It appears that the solvent plays a very important part in the action. In light petroleum no band was obtained with tetranitromethane and amylenes. The spectrum after five days and after fourteen days was the same.

Further, it would appear that there is in this way a means, not only of detecting, but also of comparing, the residual affinities of different substances; thus the different sulphides give bands of different penetrations in equal times, for example:—

	Head of band	Log-thickness <i>N</i> /100,000.	Time. Days.
<i>N</i> /10-pentamethylene sulphide		28	5
<i>N</i> /10-propyl sulphide	"	30	5
<i>N</i> /10-thioxan	"	31	5

A similar effect holds in the case of other classes of compounds.

With regard to the nature of the reaction, nitromethane was substituted for tetranitromethane with negative results. Investigations are being continued with other mononitro-compounds, in which the hydrogen atoms are replaced by chlorine and other electro-negative atoms. Dinitro- and trinitro-compounds are also being substituted. The effect of introducing electro-negative atoms into the molecule containing the centre of residual affinity is also being studied.

299. "The Relative Activities of certain Organic Iodo-compounds with Sodium Phenoxide in Alcoholic Solution. Part III. The Temperature Coefficients." By DAVID SEGALLER.

The velocity-coefficients of the following alkyl iodides, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *sec*.-butyl, *tert*. butyl, amyl, isoamyl, *sec*.-amyl, hexyl, *sec*.-hexyl, heptyl, *sec*.-heptyl, octyl, *sec*.-octyl, and cetyl iodides have been measured with sodium phenoxide in alcoholic solution at four different temperatures, and the temperature coefficients determined.

It is found that the results obtained are in good agreement with the equation of Arrhenius (*Zeit. Phys. Chem.*, 1889, iv., 226). The results show that the relative activities of the alkyl iodides are approximately independent of the temperature.

300. "Resolution of α -Anilinostearic Acid." By HENRY RONDEL LE SUEUR.

α -Anilinostearic acid has been resolved into its optically active components by crystallisation of its *l*-menthylamine salt.

d- α -Anilinostearic acid melts at 129—130°, and has $[\alpha]_D^{20} 19 + 34.7^\circ$ in solution in pyridine, and $[\alpha]_D^{40} + 18.6^\circ$ in solution in alcohol. The *l*- α -acid has also been isolated, and its properties are the same as those of its dextro-isomeride.

301. "The Conversion of d-Glucosamine into d-Mannose." (Preliminary Note). By JAMES COLQUHOUN IRVINE and ALEXANDER HYND.

In previous communications (*Proc.*, 1912, xxviii., 54; *Trans.*, 1912, ci., 1128), the authors have already described the conversion of *d* glucosamine into *d*-glucose. They have now succeeded, by a process which on first inspection seems more direct, in transforming the amino-sugar into *d*-mannose.

Methylglucosamine hydrochloride, when gently warmed with excess of benzaldehyde, passes gradually into solution when the liquid is saturated with dry hydrogen chloride. The product of this reaction is *benzylidenemethylglucosamine hydrochloride* (m. p. 205° with decomposition; $[\alpha]_D^{20} - 54.4^\circ$ in methyl alcohol), which is formed by condensation of the aldehyde with two hydroxyl groups of the sugar, and is thus comparable with the benzylidenemethylglucoside described by Alberda van Ekenstein. The compound is exceedingly unstable towards acids, and, when acted on by silver nitrite, loses not only the amino-group, but also the benzylidene residue and the glucosidic group. Chitose is thus the ultimate product of the reaction.

In order to avoid this disruption of the molecule, the amino-group was removed by the addition of excess of sodium nitrite in dilute aqueous solution. In this way the reaction of the system was kept continuously alkaline, and, although the glucosidic group was eliminated, the hydrolysis of the benzylidene residue was avoided, and thus chitose formation was excluded. During the reaction nitrogen was vigorously evolved, and a sparingly soluble product was rapidly precipitated. This proved to be a derivative of a reducing sugar, and was characterised as *monobenzylidenemannose* (m. p. 144—145°; $[\alpha]_D^{20} - 22.4^\circ$ in acetone). As the reducing group of the parent aldose is unsubstituted in this compound, the substance represents a new type of sugar derivative. On treatment with very dilute hydrochloric acid, the compound was easily hydrolysed, with the formation of *d*-mannose, which was identified by determination of the specific rotation and by con-

version into crystalline derivatives, such as methylmannoside and mannoseanilide.

The individual steps of the process outlined above appear to proceed practically quantitatively, and are summarised below:—

d -Glucosamine $\rightarrow$ methylglucosamine hydrochloride $\rightarrow$ benzylidenemethylglucosamine hydrochloride $\rightarrow$ benzylidenemannose $\rightarrow d$ -mannose.

It was shown that the formation of d -mannose as the final product cannot be attributed to the well-known action of alkali in effecting the conversion of closely related reducing sugars. Glucosamine may thus be converted into either d -glucose or d -mannose, and in one of the two processes a change of the nature of a Walden inversion must take place. The evidence at present available indicates that the change in configuration probably occurs during the decomposition of benzylidenemethylglucosamine by nitrous acid, and there seems no necessity to modify the claim made in a previous paper (*loc. cit.*) that glucosamine is a derivative of d -glucose.

302. "The Mechanism of Denitrification." By WILLIAM HULME.

A series of experiments, conducted with a view to investigate the mechanism of denitrification, showed that this reduction might be divided into two parts, namely, (1) the bacterial reduction, and (2) the enzymatic reduction.

The fermentation of similar media, one with and the other without potassium nitrate, under anaerobic conditions, showed the gas evolution to consist of nitrogen (98 per cent) and carbon dioxide from the nitrate-containing medium, and of hydrogen (70 per cent) and carbon dioxide from the nitrate-free medium. A medium containing only a very small percentage of nitrate evolved nitrogen and carbon dioxide as long as nitrate and nitrite obtained in the solution, but hydrogen and carbon dioxide appeared as soon as these had disappeared; thus the chemical agent by which the organism reduces the nitrate is nascent hydrogen.

The media were tested for enzyme action by precipitation with alcohol, drying, dissolving in water, and Chamberland-filtration, measured quantities of this solution being added to small quantities of a sterilised 1 per cent solution of potassium nitrate, and the nitrite produced being measured. The results showed a considerable reduction with the "product" obtained from the nitrate-containing flasks, whilst that obtained from the nitrate-free flasks was devoid of this reducing power.

These results were confirmed by a second series of experiments, in which the fermentation took place aerobically. The enzyme solutions in all cases were not affected by boiling.

The mechanism of denitrification may be, therefore, represented as follows:—

1. $C \dots + H_2O + \text{organism} = CO_2 + H_2 + \dots$

or—

$CH_2 \dots + O_2 + \text{organism} = CO_2 + H_2 + \dots$

where C represents the carbon of the nutrient substance.

2. $KNO_3 + E = KNO_2 + EO$
(Enzyme).

$EO + 2H = E + H_2O$

$2KNO_2 + 5H + 2CO_2 = 2KHCO_3 + 4H_2O + N_2$.

thus accounting for the large percentage of nitrogen in the gases evolved from the nitrogen-containing flasks.

303. "The Catalytic Activity of Acids. Evaluation of the Activities of the Hydrogen Ion and the Undissociated Acid." By HARRY MEDFORTH DAWSON and FRANK POWIS.

The catalytic activity of a series of acids has been examined by measurements of the velocity with which acetone passes from the ketonic to the enolic form in aqueous solutions of determinate acid concentration. The results obtained are entirely at variance with the theory that the catalysing activity of an acid is determined by its hydrogen-ion concentration, for the ratio of the reaction-velocity to the ionic concentration varies to a large extent

when the concentration of the acid is changed. The observations are, however, in good agreement with the view that both the non-ionised and ionised forms of the acid take part in the acceleration of the reaction, the actual catalytic effect being additively composed of the effects due to the two components.

The activity of the non-ionised acid diminishes rapidly as its tendency to ionise decreases; this is clearly shown by the following numbers, which express the activities n in terms of that of the hydrogen ion:—Hydrochloric, 1.77 n ; dichloroacetic, 0.50; β -dibromopropionic, 0.152; chloroacetic, 0.056; acetic, 0.0034. As yet it does not seem possible to say whether these ratios are independent of the nature of the catalysed reaction.

304. "The Configuration of the Doubly linked Nitrogen Atom. Optically Active Salts of the Semicarbazone and Benzoylphenylhydrazones of cyclo-Hexanone-4-Carboxylic Acid." By WILLIAM HOBSON MILLS and ALICE MARY BAIN.

The method which the authors used in order to investigate the configuration of tervalent nitrogen in the oximino-group (*Trans.*, 1910, xcvi., 1866) has been further employed for the examination of the configuration of the doubly-linked nitrogen in the hydrazone group, $:N.NR_1R_2$. cyclo Hexanone-4-carboxylic acid benzoylphenylhydrazone has been obtained in an optically active form by crystallisation of its quinine salt from dilute methyl alcohol. The sodium salt obtained by treating the quinine salt with sodium hydroxide was strongly dextrorotatory, having $[M]_D^{23} 38.6^\circ$.

Dextrorotatory salts of cyclohexanone 4-carboxylic acid semicarbazone (W. H. Perkin, *Trans.*, 1904, lxxxv., 427) were obtained similarly with the aid of morphine, the molecular rotations observed varying from $[M]_D^{27} 37.8^\circ$ to 27.9° in different preparations.

The active salts of both compounds showed marked autoracemisation on keeping, the loss of activity being much more rapid in the case of the semicarbazone than in that of the benzoylphenylhydrazone. The autoracemisation was checked by the addition of alkali hydroxides, sodium and potassium hydroxides being much more effective than ammonia. On acidification the activity in both cases instantly disappeared. These results can only be satisfactorily explained by regarding the molecular asymmetry of these compounds as being of the centro-asymmetric type, and due to the fact that when the carbonyl oxygen of the symmetrical keto-acid is replaced by the hydrazone residue, $:N.NR_1R_2$, the $.NR_1R_2$ group takes up a position outside the original plane of symmetry of the keto-acid. Accordingly, in these hydrazones, the three valencies of the doubly-linked nitrogen atoms do not lie in one plane, but are directed along the three edges of a trihedral angle.

NOTICES OF BOOKS.

Metallography. By CECIL H. DESCH, D.Sc.(Lond.), Ph.D.(Würzb.). Second Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

The latest results of recent investigations are incorporated in the second edition of this valuable book. The chapter on the physical properties of alloys has been much enlarged and modern work on the metallography of iron and steel is considered in some detail. The appendix, which has been carefully brought down to date, is a very useful feature. It contains details of all the binary and ternary systems of which equilibrium diagrams have been published, and in every case a reference is given to the most recent complete study of the system, or if there is any doubt about the accuracy of the work to an earlier but more trustworthy investigation.

The Absorption Spectra of Solutions as Affected by Temperature and by Dilution: A Quantitative Study of Absorption Spectra by Means of the Radiomicrometer. By HARRY C. JONES and J. SAM GUY. Washington, D.C.: The Carnegie Institution. 1913.

THE ultimate aim of the researches described in this monograph was to discover whether the free electrons of the ion have anything to do with its power of absorbing light, and for this purpose, since the absorption spectra in the region of the wave-lengths which are much greater than 0.8μ had to be studied, the grating spectrograph was useless. The radiomicrometer, however, as modified by Dr. Guy, was sufficiently sensitive to be employed for the determinations, and with its aid the absorption spectra of a number of salts were mapped. The book contains plates showing the results obtained with about fifty solutions of neodymium, uranium, and praseodymium salts, with detailed descriptions of the use of the instrument. A remarkable fact has been brought to light by the research, namely, that aqueous solutions of hydrated salts are often more transparent than pure water, and apparently combined water has less power to absorb light than free or uncombined water.

Standard Metric Equivalent Tables. Published by the Central Translations Institute, Davies Inn House, 265, Strand, W.C.

THE above collection of metric equivalent tables have been neatly printed on card, and will be found useful in the office or works where money, weights, or measures need to be changed from one system into the other. Seventy different tables are given; one side of the card is occupied with weights and measures, the other side with coinage; the tables in this form can be fixed to the side of the desk or the wall, and are much more easy for reference than when in a book.

CORRESPONDENCE.

PASSIVITY OF METALS.

To the Editor of the Chemical News.

SIR,—In the issue of your paper for November 21, 1913, there is a very interesting article by George Senter on the passivity of metals. It gives a good *resumé* of what has been done on the subject. It seems to me, however, that the valency theory has been a little overlooked. On page 751 the matter is dismissed with a few words:—"The valency theory has met with very little support during the last four or five years, and therefore need not be further considered here."

In this connection I wish to point out a rather remarkable numerical coincidence, which to my mind proves beyond dispute that the true formula for the common form of iron, as we know it, at ordinary temperatures, the α ferrite, is $\text{Fe}_{2111}-\text{Fe}_{2111}$, or a compound of ferrous and ferric atoms.

If we assume this formula, then α -ferrite would contain 60 per cent of ferrous iron. Now, the magnetic iron oxide has the formula Fe_3O_4 or $\text{FeO} \cdot \text{Fe}_2\text{O}_3$, containing 24.138 per cent of ferrous iron. The ratio between the ferrous iron in α -ferrite, and in the magnetic oxide of iron, is therefore as 60 is to 24.138, or as 1 is to 0.40230.

When Plücker compared the magnetic permeability of iron with that of its magnetic oxide, he found that the ratio was as 1 is to 0.40227.

For reasons I cannot go into at present, and which I expect to publish later, I am convinced that the magnetism of metallic iron and of its magnetic oxide must be due to the ferrous atoms alone. This led me to notice the coincidence above mentioned a little over a year ago.—I am, &c.,

HJALMAR WESTLING.

309, Union Square Buildings,
San Francisco, Cal., Dec. 6, 1913.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Bulletin de la Société Chimique de France,
Vol. xiii.-xiv., No. 18—19, 1913.

Influence of Constitution on the Thermic Properties of Binary Mixtures.—Paul Pascal and Léon Normand.—Mixtures of two substances of symmetrical structure always give mixed crystals in all proportions when the nuclear structure is the same in both compounds. Two symmetrical substances always exhibit isodimorphism when the nature of the nuclei in them is not the same. Dissymmetry of structure in the central part of the molecule (not nuclear) causes the disappearance of isomorphism, and isodimorphism appears, whatever the nuclear part of the molecule may be. Dissymmetry of nuclear structure produces the same effects as dissymmetry of the fatty central chain.

Condensation of Phenylisoxalone with Mesoxalic Ether.—André Meyer.—One molecule of mesoxalic ether condenses with 2 molecules of phenylisoxalone 1 molecule of water being eliminated:—



The product is the mesoxalate of ethyl bis-phenylisoxalone, which readily yields diethyl, diacetyl, and dibenzoyl derivatives. The ether behaves like the hydrate of the ketone $(\text{OH})_2 = \text{C} = \text{C} = (\text{CO}_2\text{C}_2\text{H}_5)_2$.

Action of Acids on Alcoholic Fermentation.—M. and Mme. Rosenblatt.—The authors have found that the following substances have no favourable action on alcoholic fermentation:—Hydrochloric, formic, acetic, propionic, *n*-butyric, sulphuric, tartaric, citric, and phosphoric acids, and monopotassium sulphate. Experiments with monopotassium phosphate, oxalate, and citrate, dipotassium citrate, and monosodium tartrate, however, show that they influence alcoholic fermentation favourably.

Determination of Methyl Alcohol and Formic Aldehyde present in Small Quantities in the same Solution.—Maurice Nicloux.—A given volume of the mixture is oxidised by bichromate and the quantity of bichromate used is determined. In a second experiment the quantity of CO_2 produced is estimated. The reactions—
 $\text{CH}_3\text{OH} + \text{K}_2\text{Cr}_2\text{O}_7 + 4\text{H}_2\text{SO}_4 =$
 $= \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{CO}_2 + 6\text{H}_2\text{O},$
 $3\text{HCOH} + 2\text{K}_2\text{Cr}_2\text{O}_7 + 8\text{H}_2\text{SO}_4 =$
 $= 2\text{K}_2\text{SO}_4 + 2\text{Cr}_2(\text{SO}_4)_3 + 3\text{CO}_2 + 11\text{H}_2\text{O},$

show that 32 mgrms. of methyl alcohol require 294 mgrms. of $\text{K}_2\text{Cr}_2\text{O}_7$ and give 44 mgrms. of CO_2 . Also 30 mgrms. of aldehyde require 196 mgrms. of $\text{K}_2\text{Cr}_2\text{O}_7$ and give 44 mgrms. of CO_2 . If x = quantity of alcohol, y = quantity of aldehyde, a = quantity of CO_2 produced by 5 cc. of the mixture which required b of bichromate $\frac{44x}{32} + \frac{44y}{30} = a$

$$\text{and } \frac{294x}{32} + \frac{196y}{30} = b.$$

Methyl Alcohol in Leaves.—Maurice Nicloux.—By the method described in the foregoing article the author has determined the amounts of methyl alcohol and of aldehyde in the products obtained by distilling leaves. His experiments showed that methyl alcohol was always present, while the presence of aldehyde was problematical. He suggests that the formation of methyl alcohol may be due to the equation $\text{CO}_2 + 2\text{H}_2\text{O} = \text{CH}_3\text{OH} + \text{O}_3$.

MEETINGS FOR THE WEEK.

WEDNESDAY, 14th.—Royal Society of Arts, 5. (Juvenile Lecture). "Electric Vibrations and Wireless Telegraphy," by R. P. Howgrave-Graham, M.I.E.E.

THURSDAY, 15th.—Royal Society of Arts, 4.30. "Indian Museums—a Centenary Retrospect," by Col. T. Holbein Hendley, C.I.E.

ERRATUM.—Vol. cviii., p. 318, col. 1, line 20, for "Distillation of Oil" read "Distillation of Coal." And, in same paragraph, "fatty oil" should read "fat coal."

THE CHEMICAL NEWS

VOL. CIX., No. 2825.

THE PHOTO-ELECTRIC BEHAVIOUR OF IRON AND THE THEORY OF PASSIVITY.*

By H. STANLEY ALLEN, M.A., D.Sc.,
Senior Lecturer in Physics at University of London, King's College.

It is not unusual to find that investigations in one branch of science serve to throw light on problems connected with some other subject. The present research was undertaken in the hope that the study of the physical phenomenon of photo-electricity might assist in elucidating the century-old problem of the nature of "passivity." The photo-electric effect here referred to is that which is known as the Hertz-Hallwachs effect (see Note). It consists in the loss of a negative electric charge or the acquisition of a positive electric charge by an insulated metal plate when the surface of the metal is illuminated. The experiments of J. J. Thomson and of Lenard have proved that the essential point in this electric change is the emission of negative electrons from the metal surface when the latter is exposed to light. In a high vacuum the current is carried by the electrons, in a gas the current is carried by ions formed by the association of the electron with one or more gaseous molecules. It is necessary to emphasise the fact that this separation of electrons is not the result of a chemical change, such as oxidation. The experiments of Elster and Geitel and many other investigators have shown that the photo-electric discharge takes place from the surface of the alkali metals in the highest attainable vacuum or in an atmosphere of argon or helium, and that such "photo-electric cells" retain their activity unchanged over periods of months or years. In this case the presence of a trace of oxygen would result in the formation of a layer of oxide which would effectively mask the phenomenon. The photo-electric current is due to the direct action of the electro-magnetic waves of light on the electrons of the metal; the energy of the light goes to increase the kinetic energy of the electron until the kinetic energy becomes sufficiently great to overcome the forces of attraction, tending to prevent the escape of the electron.

(NOTE.—We are not concerned in this paper with the photo-electric cells studied by Becquerel and Minchin, in which the potential difference between metal electrodes immersed in an electrolyte is altered by exposing one of the plates to light. Such changes may be regarded as secondary effects, while the change that we are considering is the primary photo-electric action.)

In a paper read before the Royal Society of London I have given an account of experiments on the photo-electric behaviour of iron in the active and passive state. A polished iron plate exposed to ultra-violet light rapidly loses a negative electric charge. By finding the saturation current produced when an electric field of sufficient intensity is applied, we obtain a measure of the photo-electric activity of the metal.

Dry passive iron can be obtained by using the method described by Heathcote (*Journ. Soc. Chem. Ind.*, 1907, xxvi., 899). Experiments were made with plates of Kahlbaum's sheet iron (0.2 mm. thick) and with rods of commercial iron and steel. It was found that iron which was chemically active was active in the photo-electric sense; iron rendered passive, either by the action of strong nitric acid or by use as anode in a voltmeter containing dilute sulphuric acid, showed greatly reduced activity. The photo-electric activity after treatment was less than

one half of the original value, and in some cases was too small to be detected. It should, however, be noted that iron which had been rendered passive generally showed a certain amount of photo-electric activity, so that, from the point of view of photo-electricity, passive iron shows varying, though small, degrees of activity. In these experiments the chemical activity was tested in solution, using dilute nitric acid (s.g. 1.2), whilst the photo-electric activity was measured with a dry surface. Attention must be drawn to the fact that the processes employed in changing the state of the iron were all wet processes. Muthmann and Frauenberger (*Zeit. Elektrochem.*, 1904, x., 929) state that "metals become passive on lying in the air, and their potentials (in KCl solution) assume medium values, whilst vigorous mechanical cleaning of the surface renders them active." Here the reference is to chemical activity, but the statement is equally true as regards photo-electric activity. Metals exposed to the air show "photo-electric fatigue," that is to say, their activity diminishes with an increase in the time that has elapsed since they were polished, whilst repolishing the surface gives rise to a large photo-electric current.

We appear to be justified in assuming a correlation between these two sets of phenomena, and in saying that the chemical activity and the photo-electric activity vary together. If this view be correct we see that there are degrees of activity and also of passivity, a conclusion which appears to be in accordance with the general experience of chemists. Further, we may regard the photo-electric fatigue sometimes observed with iron as a gradual passage from the active to the passive state.

We turn now to the bearing of these results on the interpretation of passivity. In view of the resemblance between the facts connected with photo-electric activity and fatigue and those relating to the passive state of metals, it is not surprising to find that the theories advanced as to the nature of the change accompanying photo-electric fatigue correspond closely with the explanations suggested for passivity (H. S. Allen, *British Assoc. Reports*, 1910; *Phil. Mag.*, 1910, xx., 572). In the table preceding the "Historical Note" these theories are given side by side.

The experiments of the author and others support the conclusion of Hallwachs that the dominant cause of fatigue is to be found in the condition of the layer of gas at the surface of the plate. So far, then, as this analogy serves, we should be inclined to attribute passivity to the surface film of gas.

We may, however, find more direct arguments in favour of the same view and against the other theories suggested.

The fact that from the photo-electric point of view different degrees of activity can be obtained from the same iron plate does not harmonise well with the idea of an allotropic change as the cause of chemical passivity; it agrees far better with the idea of a protective coating, whether of oxide or of gas, and best of all perhaps with the last named, *i.e.*, a gaseous film.

Byers (*Journ. Amer. Chem. Soc.*, 1908, xxx., 1718) in a useful summary of work done on passivity points out that "the contributors to the literature during the past ten years, with the exception of Haber and Goldschmidt, E. Müller and Spitzer, and Heathcote, unite in rejection of the Faraday view, if they fail to agree in any other particular." He regards the objections which can be urged against the existence of an oxide layer as "so convincing that we may well assent that the Faraday hypothesis may be laid to rest."

Putting on one side this view and also that which somewhat vaguely attributes passivity to the electric state of the surface, we are left to choose between the theory of, an allotropic modification of the metal and the theory of the gaseous film.

Müller and Koenigsberger (*Phys. Zeit.*, 1904, v., 413 797) found that the reflecting power of well polished iron

* A contribution to the General Discussion on "The Passivity of Metals," held before the Faraday Society, November 12, 1913.

remained unaltered when the iron was rendered passive. It was impossible to distinguish by optical means the presence of a layer of oxide, which must therefore, if present, be less than $\lambda/10$ in thickness. They support the view that passivity consists of the passage of a metallic modification of low valency into one of higher valency, but the experimental results do not seem inconsistent with the theory which attributes passivity to a gaseous film.

It has been objected to the gaseous-film theory of passivity that "a passive metal does not of necessity become active *in vacuo* (H. L. Heathcote, *Journ. Soc. Chem. Ind.*, 1907, xxvi., 899; J. N. Friend, "The Corrosion of Iron and Steel," p. 190). But it must be remembered that experience has repeatedly shown the impossibility of removing films of condensed gas from the surfaces of solid bodies merely by placing them in a high vacuum (compare F. S. Spiers, *Phil. Mag.*, 1900, xlix., 40; H. S. Allen, *Ibid.*, 1903, vi., 706; and also J. N. Friend, "The Corrosion of Iron and Steel," chap. v.).

If, then, we may regard the photo-electric behaviour of the metal as the criterion by which we may decide between the two principal theories, we are led to the conclusion that passivity is to be attributed to the condition of the gaseous film on the surface of the metal.

Theories of Photo-electric Fatigue.

Theories of Passivity.

- | | |
|--|---|
| 1. A chemical change, such as oxidation of the surface. | Formation of a protective film of oxide.
Formation of a layer of nitride. |
| 2. A physical change of the metal itself. | An allotropic modification of iron. "Passive" iron trivalent; "active" iron, divalent. |
| 3. Formation of an electrical double layer. (Lenard.) | "A permanent electric state of the surface." (Herschel.) |
| 4. A disintegration of the metal due to the expulsion of electrons by light. (Ramsay and Spencer.) | |
| 5. A change in the surface film of gas or in the gas occluded in the metal. (Hallwachs.) | An adherent surface film of gas which protects the iron from the action of the acid (see Note). |

(NOTE.—An alternative form of this theory is to regard the normal state of pure iron as passive, and to attribute activity to hydrogen, probably in the ionic state.)

Historical Note.

In the more recent literature of "passivity" the oxidation theory is rightly attributed to Faraday, but the fact that the gaseous-film theory may equally claim the authority of his name has been overlooked. Faraday in his letter communicating the experiments of Schoenbein to the *Philosophical Magazine* (1836, [3], ix., 57) writes: "My strong impression is that the surface of the iron is oxidised, or that the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation."

In the August number (p. 122) he reviews some earlier observations on the peculiar or altered state of iron. Westlar "attributes the effect to the assumption of a negative electric state by the part immersed, the other part of the iron having assumed the positive state." Sir John Herschel "attributes the phenomena to a certain permanent electric state of the surface of the metal." Professor Daniell suggests that the effect is due to a difference in the mechanical structure of the surface of the iron.

Thus even at this period we have representatives of the principal theories that have been advanced to account for passivity.

Schoenbein (*Phil. Mag.*, 1836, [3], ix., 259; 1837, x., 172) disagrees with Faraday's view. He says: "It is evident that the different action of the same nitric acid on iron is caused by a certain electrical state of the metal." Again, "That the iron (used as electrodes in nitric acid) is not partially oxidated is evident from its unchanged metallic lustre, as also from the proportions of gas given off at both wires, which I found according to several measurements to be as 1 to 2." In the second paper he directly attacks the oxidation theory, bringing forward many objections to it, and concludes: "All the reasons above given decide me to suppose that Faraday's views concerning the passive state of the iron do not explain it satisfactorily." In the same number Faraday replies emphasising the guarded character of his suggestion, which need not imply an actual oxidation but "a very delicate equilibrium of forces" where there is "association without combination." He agrees with Schoenbein that a satisfactory explanation of passivity has not been reached.

Thus it will be seen that Faraday's more guarded view is essentially the same as that which attributes the effects to the peculiar condition of the gaseous film at the surface of the metal.

To sum up our conclusions, we may say that iron which is chemically active shows large photo-electric activity, while processes which render iron passive greatly reduce this activity. These facts are in good agreement with the theory, which as well as the oxidation theory must be attributed to Faraday, that the cause of passivity is to be found in the condition of the gaseous layer at the surface of the metal.

THE CONSTITUTION AND STRUCTURE OF THE ELEMENTS.

By HAWKSWORTH COLLINS.

THE most regular row in the Periodic Table is the second containing the elements sodium, magnesium, aluminium, silicon, phosphorus, sulphur, and chlorine; and it must have been this row which was chiefly instrumental in producing the Periodic observation. A number of facts with regard to these 7 elements are now given in tabular form, followed by four observations upon them.

TABLE I.

Element.	Nearest At.wt. whole number.	Number of parts the at. wt. Max. is divided valency. into.	I	I
Na 23.00	23		1	1
Mg 24.32	24 = 23 + 1	2	2	2
Al 27.1	27 = 23 + 1 + 3	3	3	3
Si 28.3	28 = 23 + 1 + 3 + 1	4	4	4
P 31.04	31 = 23 + 1 + 3 + 1 + 3	5	5	5
S 32.07	32 = 23 + 1 + 3 + 1 + 3 + 1	6	6	6
Cl 35.46	35 = 23 + 1 + 3 + 1 + 3 + 1 + 3	7	7	7

1. Whenever the atomic weight of one of these elements is nearer to an even whole number its maximum valency is even; and whenever it is nearer to an odd whole number its maximum valency is odd.

2. A symmetrical arrangement of the whole numbers is possible, with a portion 23 in each.

3. The number of parts each whole number is divided into corresponds exactly with the valency of each.

N.B.—It is a chemical fact that one valency emanates from a mass of 23 (Na). It is also a fact that one valency emanates from a mass of 1 (H). Again, it is a fact that 2 valencies emanate from a mass of 4 (He). Therefore it is perfectly logical to say that, in the case of P, for instance, its 5 valencies emanate from the 5 portions 23, 1, 3, 1, and 3; with similar remarks for the other 6 elements.

4. When there is no portion (1 + 3, helium) present the

element is metallic, as in Na and Mg; but when this portion is present the element is non-metallic.

The above are four independent and exact observations to which there is no exception. The mathematical probability that any one of the four has happened by accident is $1 : 2^7$. Therefore the probability that the four observations together are the result of an accident is $1 : 2^{28} = 1 : 268,435,456$.

The following six observations are also important:—

1. The atomic weights of all the 7 elements are either equal to or *greater than* the nearest whole numbers. This fact distinctly suggests that some impurity is liable to be present which causes some of the atomic weights to appear greater than they really are.

2. If helium could be given off from chlorine (35.46) with 7 valencies a portion would be left of atomic weight 31.46 with 5 valencies. Phosphorus (31.04) has 5 valencies.

If helium could be given off from phosphorus a portion would be left of atomic weight 27.04 with 3 valencies. Aluminium (27.1) has 3 valencies.

If helium could be given off from aluminium a portion would be left of atomic weight 23.1 with 1 valency. Sodium (23.00) has 1 valency. Again, if helium could be given off from sulphur (32.07) with 6 valencies, a portion would be left of atomic weight 28.07 with 4 valencies. Silicon (28.3) has 4 valencies.

And, if helium could be given off from silicon, a portion of atomic weight 24.3 would be left with 2 valencies. Magnesium (24.32) has 2 valencies.

3. Sir J. J. Thomson's X_3 could be given off from Cl, P, and Al.

4. Of all the metals sodium is *the* most likely to be a constituent part of other elements, since it is the most widely distributed metal.

5. The fact that the atomic weight of Cl is given as 35.46 instead of 35 does not upset the above argument at all, because we are considering the nearest whole numbers to the atomic weights.

6. It is quite possible that an atom of chlorine may have a special aptitude for condensing an abnormally large amount of protyle.

In the radio-active elements, whenever an atom of helium is given off with 2 valencies, the main portion loses 2 valencies; therefore it is evident that the helium atom was joined to the rest of the element by a non-chemically-evident force.

Besides, if it had been united with the remainder of the element merely by 1 or both of its valencies, the two parts would together have formed a chemical product, or molecule, and not an element. For instance, radium with 2 valencies splits up into helium with 2 valencies, and niton with no valency. Therefore helium was not united to niton by a valency, but by some other force; otherwise radium would be a chemical compound, niton-helium.

It follows from this that non-chemically-evident forces have been discovered by reasoning.

This deduction, together with all the above facts and observations, demonstrates that the constitution and structures of these seven elements is as follows, where the thin lines denote non-chemically-evident forces and the thick lines denote valencies. The structure of the portion 23 cannot be considered at present. (See Table II.).

The significance of this number 23 is now going to be extended. There are 83 elements recognised by the International Committee. The 10 of less atomic weight than 23 cannot come into the argument, and 14 others, La, Ce, Nd, Pr, Sa, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, are rare elements, which cannot be considered in any way in relation to the others, because they cannot be placed in any satisfactory order in the Periodic Table. There are, therefore, 59 elements left for consideration. Thirty-four of the 59, *i.e.*, more than half, are concerned in Table III. and in the preceding matter.

† The number 23 has an evident predominance in this table. The first 9 pairs are connected by the Periodic Observation. Hg is especially connected with Ag in

TABLE II.

Sodium	Na
Magnesium ..	Na—H
Aluminium ..	Na—H—H ₃
Silicon	Na—H—H ₃ —H
Phosphorus ..	Na—H—H ₃ —H—H ₃
Sulphur	Na—H—H ₃ —H—H ₃ —H
Chlorine	Na—H—H ₃ —H—H ₃ —H—H ₃

mineralogy, and Cb with Ti. Cu is evidently connected with Ca, since they are both dyads, although the Periodic Table stands in the way. The chemical compounds of Rh are analogous to those of Fe, and the compounds of Ru are *exactly* analogous to those of Mn.

Molybdenite (MoS_2) is especially found with cryolite (Na_3AlF_6) in Greenland. This fact would not be remarkable if one or both were common minerals, but they are both rare. The molecule MoF_6 is well known. Ga is *always* found with Al. The matrix of the element Ga is said to be "Si-Al-minerals from which most of the Na has been dissolved." (This statement undoubtedly suggests that Ga has been formed from the extracted Na). These facts show the connection between Mo, Ga, Al, and Na.

The last two elements, As and Cr, have no evident connection either in the Periodic Table or Mineralogy, but since their at. wts. are in accordance with the general rule about even and odd numbers, they are given here.

Now, owing to the discovery of the fact that protyle and X_3 can be given off from all sorts of substances, *it must be necessary to redetermine the ratio of the atomic weights of oxygen and hydrogen, after expelling all traces of these impurities.*

Another source of error exists in the fact that it is very difficult, or perhaps impossible, to entirely separate elements that are chemically alike. For instance, it is very difficult to obtain Cb free from Ti. The atomic weight of Cb is given as 93.5. Taking into consideration all the foregoing arguments, surely it cannot be very outrageous to say that all available evidence shows that the atomic weight of Cb is 94, and that of Ti 48, so that the difference is $46 = 2 \times 23$.

Again, suppose it is found that the 0.46 of the atomic weight of Cl (35.46) is due to protyle and X_3 , then there will be large errors in those atomic weights, which are calculated from Cl.

In order to complete the argument with regard to pairs of like elements, it is necessary to give another table showing that the atomic weights of 8 pairs of elements have a difference of 90 (zirconium), which element can be shown to contain 3 atoms of sodium in its constitution. (Table IV.).

Zirconium (90.6) is especially connected in mineralogy with most of the above, and the elements of each pair are connected by the Periodic Observation.

It is much more likely that the differences are exactly the same than that they are nearly the same.

The three last tables concern 45 out of the 59 elements (*i.e.*, more than three-quarters) available for the argument.

It has now been shown that "the numbers 23 (Na) and 90 (Zr) connect the atomic weights of all or nearly all pairs of like elements." This is not intended to be the second main principle in the constitution and structure of the elements, which was referred to in the paper published in the CHEMICAL NEWS, November 14; but it must temporarily take the place of that principle, for it has been found impossible to get all the evidence required into a short paper.

TABLE III.

Element.	At. wt.	An element with which the former is especially associated in chemistry or mineralogy or both.	At. wt.	Difference in at. wt. of the associated elements.	Deductions.
Cadmium	112.40	Zinc	65.37	47.03 = 2 × 23.515	Cd = Na ₂ Zn
Cæsium	132.81	Potassium ..	39.10	93.71 = 4 × 23.427	Cs = Na ₄ K
Rubidium	85.45	Potassium ..	39.10	46.35 = 2 × 23.175	Rb = Na ₂ K
Indium	114.8	Gallium	69.9	44.9 = 2 × 22.45	In = Na ₂ Ga
Selenium	79.2	Sulphur	32.07	47.13 = 2 × 23.565	Se = Na ₂ S
Iodine	126.92	Chlorine	35.46	91.46 = 4 × 22.865	I = Na ₄ Cl
Antimony	120.2	Vanadium	51.00	69.2 = 3 × 23.066	Sb = Na ₃ V
Xenon	130.2	Krypton	82.92	47.28 = 2 × 23.64	Xe = Na ₂ Kr
Niton	222.4	Xenon	130.2	92.2 = 4 × 23.05	Nt = Na ₄ Xe
Mercury	200.6	Silver	107.88	92.72 = 4 × 23.18	Hg = Na ₄ Ag
Columbium	93.5	Titanium	48.1	45.4 = 2 × 22.7	Cb = Na ₂ Ti
Copper	63.57	Calcium	40.07	23.50 = 1 × 23.50	Cu = NaCa
Molybdenum	96.0	Aluminium	27.1	68.9 = 3 × 22.97	Mo = Na ₃ Al
Gallium	69.9	Sodium	23.00	46.9 = 2 × 23.45	Ga = Na ₃
Rhodium	102.9	Iron	55.84	47.06 = 2 × 23.53	Rh = Na ₂ Fe
Ruthenium	101.7	Manganese	54.93	46.77 = 2 × 23.385	Ru = Na ₂ Mn
Arsenic	74.96	Chromium	52.0	22.96 = 1 × 22.96	

(Not associated).

TABLE IV.

Tin	119.0	Silicon	28.3	90.7	Sn = ZrSi
Gold	197.2	Silver	107.88	89.32	Au = ZrAg
Osmium	190.19	Ruthenium ..	101.7	89.2	Os = ZrRu
Iridium	193.1	Rhodium	102.9	90.2	Ir = ZrRh
Platinum	195.2	Palladium	106.7	88.5	Pt = ZrPd
Radium	226.4	Barium	137.37	89.03	Ra = ZrBa
Tungsten	184.0	Columbium ..	93.5	90.5	W = ZrCb
Xenon	130.2	Argon	39.88	90.32	Xe = ZrA

The second main principle, which remains to be further demonstrated, is "sodium takes a prominent part in the formation of all elements of greater atomic weight than itself."

The constitution and structure of the elements, as here given, was obtained ten years ago, and so was not influenced in the slightest by the modern discoveries regarding the splitting up of the radioactive elements. Therefore these discoveries prove the correctness of this reasoning.

A STUDY OF VARIOUS SPECIES OF FUNGI.

By H. T. F. RHODES.

AN analysis was made of four well-known species of fungi. The samples were obtained in October, November, and December. A short description of each variety will not be out of place.

The Common Earth Ball (*Scleroderma vulgare*).

The earth ball is small in the first stage, but is often 10 inches in circumference when full grown. Its outer surface is horny and of a dirty white colour, and the inner portion of a bluish grey. When this fungus begins to decay the inner portion becomes powdery, which is due to the formation of spores. It is not suitable for human consumption.

The Common Polyporus (*Polyporus versicolor*).

The above is too well known to require description. It grows on most dead trees.

The Edible Boletus.

The edible *Boletus* is a fungus about 3 inches in diameter. It has a brown cap and yellow gills. It is spongy and gelatinous to the touch.

The Sulphur Tuft (*Agaricus fascicularis*).

The Sulphur Tuft is generally 2 inches in diameter, with a yellow cap and green gills. This fungus is one of the few poisonous varieties.

An outstanding feature of the analysis is the high percentage of nitrogen in these vegetables. This makes their food values an important factor. It is peculiar that the *Agaricus campestris* is, in the majority of cases, the only species of which use is made for human consumption, as there are many other species which are as palatable and in many cases quite as nutritious. But a still more important point is the use of the growths as feeding stuff for cattle. Many of the species which are unpalatable to human beings would probably be consumed quite readily by animals. It is a pity that year after year such large quantities of useful material should be allowed to rot. It is commonly supposed that the common mushroom is the only non-poisonous variety, but this is a fallacy, as certainly not more than 2 per cent of the English species are poisonous.

The general method of the analysis was as follows:—

The Moisture.

Ten to thirty grms. of the sample according to the species were dried in an air oven at 70 to 90° C., until they ceased to lose weight. The results were as follows:—

	Per cent.
<i>Scleroderma vulgare</i>	84.30
The edible <i>Boletus</i>	87.93
<i>Agaricus fascicularis</i>	88.14
<i>Polyporus versicolor</i>	54.31

These results must not be taken as absolutely indicative, as the moisture varies according to the size of the fungus, the moisture of the ground, and other conditions.

The Ash.

One to five grms. were burnt up in a platinum crucible and reduced to a perfect ash, then cooled under a desiccator and weighed:—

	Per cent.
<i>Scleroderma vulgare</i>	12.22
The edible <i>Boletus</i>	10.75
<i>Agaricus fascicularis</i>	6.60
<i>Polyporus versicolor</i>	5.92

The ashes were very hygroscopic, yellow while hot, green when cold.

The Crude Fibre.

Estimations of crude fibre were made by the acid and alkali method, 1 grm. of the fat-free sample being used in each case. The results were as follows:—

	Per cent.
<i>Scleroderma vulgare</i>	19.20
The edible <i>Boletus</i>	10.12
<i>Agaricus fascicularis</i>	10.33
<i>Polyporus versicolor</i>	20.41

It will be noticed that the crude fibre is very high in the first and last case and somewhat excessive in the other two. This is produced to some extent by the fibrous layer on the caps of the *Boletus* and *Agaricus fascicularis*, and also by the stem, but as these portions are both removed before consumption it is not of much importance. In the case of the *Polyporus versicolor*, the woody matter is not of such a superficial nature, as it partially partakes of the woody nature of the trees on which it grows. It may be broadly stated that on this account the *Polyporus* varieties are unsuitable for human or animal consumption. This statement applies in a somewhat modified degree to the *Scleroderma vulgare*, but much of the woody matter may be removed from this species by peeling off the outer husk.

The Nitrogen.

Estimations were made by Kjeldahl's process. One to two grms. were treated with 25 to 30 cc. of Nitrogen free H_2SO_4 , 10 grms. of potassium hydrogen sulphate were added, and after an hour a fragment of copper sulphate. The mixture was heated until the carbonaceous matter was destroyed. The acid was diluted with 250 cc. of distilled water, made alkaline with caustic potash, and steam distilled into 50 cc. of $N/5 H_2SO_4$. The results were as follows:—

	Per cent.
<i>Scleroderma vulgare</i>	5.29
The edible <i>Boletus</i>	7.02
<i>Agaricus fascicularis</i>	3.18
<i>Polyporus versicolor</i>	2.26

$\times 6.25 = \text{Protein.}$

<i>Scleroderma vulgare</i>	33.06
The edible <i>Boletus</i>	43.85
<i>Agaricus fascicularis</i>	19.87
<i>Polyporus versicolor</i>	14.12

The high percentage of protein will be noticed. It is of course of the highest importance from the point of view of nutriment.

The Fat.

One to two grms. of the finely ground sample were treated with petrol ether in a Soxhlet apparatus for 24 hours. The oils were very viscid at the ordinary temperature. In the case of the edible *Boletus* the oil was of a yellow colour, and in the other cases brown. In many cases the oils developed a most unpleasant odour if left exposed to the air for two or three days.

	Per cent.
<i>Scleroderma vulgare</i>	2.00
The edible <i>Boletus</i>	3.30
<i>Agaricus fascicularis</i>	3.82
<i>Polyporus versicolor</i>	1.23

Owing to a shortage of samples it was unfortunately im-

possible to make estimations of the carbohydrates, but more work will be in progress shortly in that direction.

The analysis was made on the dry samples in all cases. The above results compare very favourably with the analysis of dried lentils which appears in the "Scientists' Note-book and Diary for 1913," as follows:—

	Per cent.
Moisture	8.4
Protein	25.7
Fat	1.0
Ash	5.7
Carbohydrates	59.2

The lentil has a greater quantity of protein than the large majority of vegetables or fruit, and it will be noticed that its protein value is considerably lower than that of a dried sample of the edible *Boletus*. From the preceding analysis it is reasonable to assume that fungi can in many cases be used as a very satisfactory article of diet, a fact which until quite lately has been absolutely ignored, and is not at the present time by any means universally accepted. It has been suggested for use as food for cattle and other animals. It is not suggested that it should replace cotton and linseed cake, &c., but augment them.

A NEW STEAM GENERATOR.

By J. ALAN MURRAY, B.Sc.

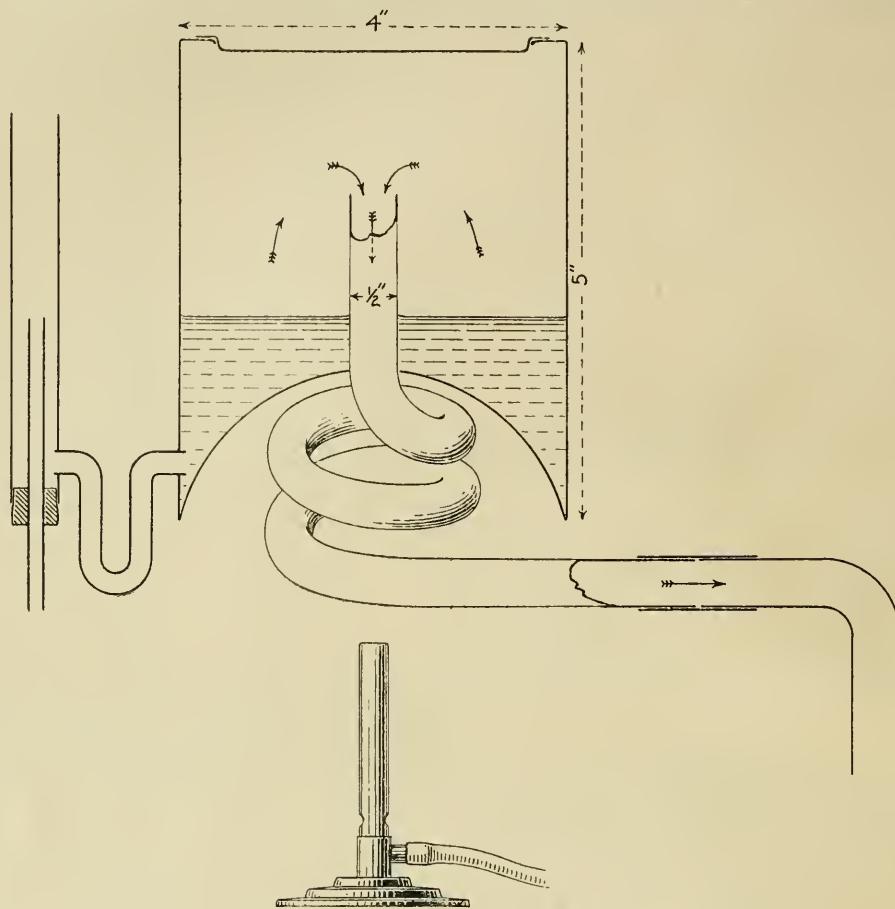
THE accompanying sketch shows the essential parts of a form of steam generator which has given very satisfactory results in my laboratory. The apparatus consists of a copper cylinder 5 inches high by 4 inches in diameter. It is fitted with an air-tight lid like that of a caustic soda tin, and the bottom is externally concave. A copper tube, $\frac{1}{2}$ inch in diameter, which passes through the bottom and projects to within about $1\frac{1}{2}$ inches from the top, is coiled in two folds in the hollow outside the bottom. A space of about $\frac{1}{2}$ inch is left between the two folds of the coil, and also between the upper fold and the bottom of the cylinder to allow of the proper spread of the flame. The parts of the apparatus are brazed together.

Water is introduced into the cylinder and maintained at constant level by means of a side tube arrangement of the usual kind. The connecting tube is bent to prevent the too sudden access of cold water, which otherwise might cause the water to cease boiling. The steam which passes through the coil becomes superheated without any increase of pressure and may be used for many different purposes. The following results were obtained when the heat was supplied by means of an ordinary Bunsen burner, and the vapour was led into a small steam bath which measured $9 \times 4\frac{1}{2} \times 4\frac{1}{2}$ inches and weighed just under 1 lb.:—

0 minutes	Gas lighted.
3 "	Water in cylinder boiled.
7 "	Temperature in bath, $100^\circ C$.
11 "	" " $120^\circ C$.
14 "	" " $138-141^\circ C$.

The variation in the maximum temperature was attributed to the occasional inflow of cold water into the cylinder.

The rate of evaporation of water in basins placed on the bath was greatly accelerated. It was also found that water in a beaker covered with a watch-glass boiled when the vessel was completely immersed in the vapour, *i.e.*, hanging by the tip from the ring, but not if any considerable portion of it protruded. As the boiling takes place quietly and steadily this is a convenient method of heating liquids that are apt to froth or to bump and break the



(When in use the apparatus is supported on a tripod not shown in the diagram).

beakers. It has been successfully employed, for example, in the estimation of crude fibres.

The chief advantage of the apparatus, however, probably lies in the fact that it may be used to apply steam to baths, ovens, &c., made of zinc or tin instead of copper, and a considerable saving of cost can be thus effected. The apparatus itself can be made for about £1. It should also prove handy in laboratories that are so fortunate as to have steam "laid on," for it frequently happens that the supply fails at night or in vacation times. Of course one does not always want a temperature above 100° C., but the apparatus can be used as an auxiliary method of heating. All that is necessary is that the bath or oven should be provided with a tubular to fit the delivery pipe of the generator. This tubular can be closed with a cork when the generator is not in use. No solder or lute of any kind is required if the tubular fits the pipe fairly closely. One steam generator may, therefore, be used to heat several pieces of apparatus in turn. As it is small and easily disconnected it can be moved about the laboratory as required. To adapt it for these various purposes a collar, *i.e.*, a piece of copper tube of diameter slightly larger than the delivery pipe, is brazed on to the end of the latter, and another piece of the same size as the delivery pipe is bent at a right angle and fits into the collar. This is used as a connecting tube. It is not soldered into the collar, but merely fits in tightly, and so can be turned down or up or in a horizontal direction. By this means the generator can be readily accommodated to many different pieces of apparatus.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

BORON IN THE HUMAN ORGANISM.

There is no simple element that is not contained in the human organism. Quite recently M. Gabriel Bertrand, of the Pasteur Institute, has shown that our tissues contain boron. Dr. Roux now describes the method imagined by MM. Gabriel Bertrand and Agulhon to estimate the extraordinary small proportions of boron and boric acid that are normally found in all the parts of the animal and vegetable organism. These methods enable the estimation of the weights of metalloid as small as the half-thousandth of a milligram. The method is based on the employment of little tests of turmeric. Vegetables contain from 100 to 1000 times more boron than that contained in animal tissues. The new method of analysis will facilitate the study of the accumulations of boron, and will allow it to be seen what is its physiological rôle.

THE FORMATION OF THE PLANETARY SYSTEM.

In 1880 the celebrated astronomer Payet searched how a spherical nebula, with a density increasing as far as the centre, could give birth to the primitive sun imagined by Laplace. In a communication made by M. Bigourdan to the Academy of Sciences, M. Emile Belot, Director of the State Manufactories, has taken up again the idea of Fayet, and has generalised it by applying it to the indefinite cylindrical layers in rotation, assembling whirlwind, or

vortex formations. It is then found that in such a spherical nebula there exist three remarkable cylindrical layers: one of which contains the maximum of centrifugal power; the third possesses the maximum tangential speed. The rays of these three layers are very much in the same relation to each other as the distance of Jupiter (the maximum mass) from Saturn (the mass of minimum density), and that which, in the solar system, separates the region of the planets with a direct rotation from those which move with a retrograde rotation.

THE FREQUENCY OF EARTHQUAKES.

The late English savant Milne, whose works on seismology are so well known, recently published a general catalogue of the destructive earthquakes registered since the beginning of this era. He found the principal elements of his work in the catalogues drawn up by Alexis Perrey, of Dijon. Without taking into account the little irregular shocks which are generally but a repercussion of intense and far off earthquakes, Milne reaches the total of 4000 seismic shocks. Up till the year 650 A.D. were noticed; that is to say, about 14 per century. From 650 to 1650 the total number of cataclysms reached 1099, or about a little more than one earthquake per year. From 1650 to 1840 the number of important shocks goes up to 11 per year. From 1840 to 1849 the annual average is 18, and it goes up to 31 for the period from 1850 to 1859. In these statistics there are numerous voids, but it may be supposed that from 1850 all the earthquakes of any importance are known. Now, from 1850 to 1898 no less than 1521 destructive earthquakes were counted; that is to say, about 31 per year, and the difference between the annual maximum does not exceed 2.8 per cent per annum of the total. The mundane seismic activity was then sensibly constant during the second half of the nineteenth century. The International Seismological Association, which every year publishes the statistics of earthquakes of a certain intensity, registers about 27,000 shocks for the years between 1900 and 1909. The number of earthquakes varies then from 250 to 300 per year, which is a considerable figure, seeing that the shocks that occur on the sea and in uninhabited regions are not taken into account.

PORTABLE WIRELESS TELEGRAPHY.

It is known that the Hertzian waves spread in all directions and to very great distances. Branley's coherer and different detectors enable them to be received easily. If one of these receptive apparatus is joined to a telephone, each signal of the wireless telegraphy produced by a spark more or less long is translated into the telephonic apparatus by a more or less prolonged tone. But these instruments are rather cumbersome. An engineer, Justin Landry, has just presented before the Astronomical Society of France a pocket apparatus that is destined to receive wireless telegraphic signals. This tiny detector, formed by an inoxidisable crystal and a very hard steel point, is fixed to the bottom of a telephonic receptor. It has no attached coil, and in the majority of cases it is not necessary to have a hold on the ground. Trials have been made at the foot of the Eiffel Tower and as far as the furthest corners of France. The most diverse feelers have been employed. In Paris the mere contact of the isolated wire with any metallic body is sufficient, whether it be a simple curtain rod, or the gas and water pipes, or the framework of a motor-car or motor-bus. At distances varying from 40 to 50 kilometres from Paris, the roof gutters, spouts, the railings, garden tools (such as spades), and, still better, steel frame umbrellas with wooden handles, enable one to assure an excellent reception of the signals from the Eiffel Tower. Further away, at a distance of 1000 kilometres telephonic wires or well arranged antennæ have allowed radiotelegrams to be very well received. M. Landry has signalled from antennæ or feelers that are always and everywhere to be found at hand; that is to say, trees. They have a considerable faculty of reception. At 80 kilometres from Paris a contact taken on a tree at a height

of 2 or 3 metres with a pin or a gimlet pushed in to a certain depth, a hold on the ground managed by fixing the blade of a knife into the earth, have enabled meteorological despatches to be heard, and also the time signals and the radio-telegrams that the Eiffel Tower transmits every day all over the world. Atmospheric disturbances, such as storms, &c., also influence greatly the detectors. A characteristic noise of molten metal falling into water reveals these disturbances. It may be said that the lightning flashes are, as it were, heard long before they are seen. Colonel Renard has drawn attention to the services that the reception of meteorological radio telegrams might render to aeronauts and aviators.

ORIGIN OF MILDEW IN PLANTS.

Up till quite lately every one imagined that the rust or mildew of cereals and other plants was due to an exterior contamination caused by parasitic fungi belonging to the uredine group. However, in making wheat or corn germinate and grow in closed aseptic rooms, Prof. Eriksson, of Stockholm, announced fifteen years ago that the rust might appear at a given moment on the plants thus protected; whence it was naturally concluded that the parasite must already exist in the grain of corn itself. Divers experiments by M. Blaringhem, the results of which have been communicated to the Academy of Sciences by Prof. Guignard, have, on several points, confirmed the opinion expressed by Eriksson as to the origin of mildew. These experiments more especially concerned hollyhocks, the leaves of which are attacked by a special kind of rust. In taking all the possible and desirable precautions for this kind of experiment, M. Blaringhem has observed that if the seeds of this plant previously sterilised are put to germinate in places in which are also placed determined quantities of glucose and saccharose, the rust makes its appearance on the plantules, whereas it does not appear in the absence of these nutritive matters. The manifestation of the parasitary disease would then appear to be subordinate to certain conditions of environment. In any case there seems to be no doubt but that this rust is hereditary.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 4th, 1913.

Prof. W. H. PERKIN, LL.D., F.R.S., President,
in the Chair.

THE PRESIDENT referred to the loss sustained by the Society through the death of James Tudor Cundall (Edinburgh) and Thomas Ebenezer Pye (Chichester).

THE PRESIDENT announced that the Society had replenished its stock of apparatus and reagents for the use of Fellows making experiments at the meetings of the Society. Fellows can obtain a list of the apparatus and reagents by applying to the Assistant Secretary.

Certificates were read for the first time in favour of Messrs. Sydney George Clifford, 3, Norman Villas, East Dulwich, S.E.; Thomas Alexander Davidson, 57, Strathyre Avenue, Norbury; Thomas Eynon Davies, B.Sc., 25, Trevor Street, Aberdeen; James Stanley Hale, Principe 4, Bilbao, Spain; Alfred John Leigh, B.Sc., Duff House, Banff; Archibald Macpherson, 51, Keir Street, Glasgow; Frederick Arthur Makin, The Nest, Taunton Road, Ashton-under-Lyne; Thomas Morris, 53, Poolstock, Wigan; Raymond William Nichols, Central Experimental Farm, Ottawa, Canada; William Julian Odum, B.A., Ardmore, Bray; Charles Alfred Stanip, Passer's House, Eltham; Eustace Ebenezer Turner, R.Sc., 5, Queen's Gate Villas, South Hackney, N.E.

Messrs. Harold King and W. B. Tuck were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared as duly elected:—Parmanand Mewaram Advani, M.A., B.Sc.; Richard Watson Askew, B.A.; Sankar Rao B. Badami, M.A.; Alan Milsom Bailey; Stanley Charles Bate, B.Sc.; Alan Hamilton Bateman; Charles Maurice Berlein, B.A.; Arthur Bicknell, B.Sc.; Augustus Pearce Llewellyn Blaxter, B.A.; Adhor Krishna Bose; Arthur Bramley, B.Sc.; Arthur Joseph Brearley, B.A.; George Bernard Butler; Bertram Campbell, B.Sc.; Norman Phillips Campbell, B.A.; Frederick George Carter; Santi Pada Chowdry; Francis William Clark; Herbert Stoddard Coleman; Thomas James Drakeley, B.Sc.; Mohamed Shams Eldin, B.Sc.; Cyril Duncan Fuller; Charles John Dickenson Gair; Stanton Gibson, B.Sc.; Richard Hargreaves, B.A.; Alexander Houghton Hay; George Alfred Hebben; Richard Pendarves Hodges; William Francis Holleley; Charles Huxtable; Alexander Hynd, M.A., B.Sc.; William Johnson, B.Sc.; Harold Bramfield Jones; Ghulam Rasul Khan, B.Sc.; Sidney Oliver Leivesley; William John Lewis; Percival James Lycett; Frank Clifford Marchant; Kunerji Gosai Naik, M.A., B.Sc.; John Allen Nichols; John Thomas Pattison; Wilfred Roberts Powell, B.A.; Henry Edward Findlater Pracy; Benedict Hugh Rolfe, M.A.; Philip Howard Stott; John McArthur Stuart; John Algernon Lacy Sutcliffe; Harold Frank Tayler; Robert Tennant; Henry Walker; Bertie Mandel Welch; Henry Wood.

Of the following papers those marked * were read:—

*305. "The Action of Sulphuric Acid on Copper." By (the late) JAMES TUDOR CUNDALL.

It is commonly supposed that the mutual action of copper and sulphuric acid may be represented by the production first of cupric sulphate and nascent hydrogen, which latter produces more sulphuric acid and from it sulphur dioxide.

The present investigation shows that cuprous sulphate, rather than cupric sulphate, is one of the primary products, as may easily be tested by pouring off the sulphuric acid at any stage of the reaction through a Gooch filter into water, when a precipitate of finely divided copper is produced. This result is best obtained when the sulphuric acid is slightly diluted with water, for when hot or concentrated acid is used, the cuprous sulphate acts on the acid almost as soon as formed, giving cuprous sulphide and cupric sulphate. This last action also takes place, but more slowly, with cooler acid.

The cuprous sulphide then, as Pickering found, becomes oxidised to cupric sulphide and cupric sulphate with evolution of sulphur dioxide, and thereafter the cupric sulphide gives the sulphate, with a further evolution of gas.

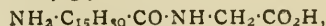
*306. "Synthesis of Polypeptides from the Higher Fatty Acids." By ARTHUR HOPWOOD.

Although so many polypeptides have been prepared lately, only one has been obtained from the higher fatty acids. The author has therefore synthesised several dipeptides from palmitic and stearic acids, so that their properties could be ascertained and compared with those of the degradation products of the proteins.

α -Bromopalmityl chloride, $C_{15}H_{31}Br \cdot COCl$, prepared from α -bromopalmitic acid and thionyl chloride, is a colourless oil, which crystallises on cooling, and boils with decomposition at about $215^{\circ}/20$ mm.

α -Bromopalmitylglycine, $C_{15}H_{31}Br \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$, prepared by condensing α -bromopalmityl chloride with glycine, crystallises in colourless plates, melting at $118-121^{\circ}$.

α -Aminopalmitylglycine,—



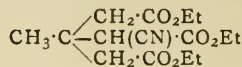
prepared by heating α -bromopalmitylglycine with ammonia, crystallises in colourless hexagonal plates, melting and decomposing at $222-224^{\circ}$.

Similar dipeptides have been prepared by coupling α -bromopalmityl or α -bromostearyl chloride with alanine or leucine, and heating the products with ammonia. Isomerides of these dipeptides have also been prepared by the action of ammonia on the products obtained by condensing α -bromoacetyl, α -bromopropionyl, or α -bromoisobutyryl chloride with α -aminopalmitic or α -aminostearic acid.

The dipeptides derived from palmitic and stearic acids are tasteless, or slightly bitter, crystalline solids melting and decomposing at above 200° . They are insoluble in water, alcohol, ether, or benzene, but dissolve in hot dilute mineral acids or alkali hydroxides. They form characteristic crystalline compounds with 8-naphthalenesulphonyl chloride, and, like the natural proteins, the dipeptides give white amorphous precipitates with phosphotungstic acid.

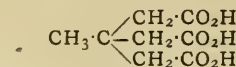
*307. "A New Series of Ring Compounds." (Preliminary Note). By RICHARD MOORE BEESLEY and JOSEPH FIELD THORPE.

The fact that the ethyl ester of labile β -methylglutaconic acid, which can be readily obtained from ethyl acetoacetate (*Trans.*, 1912, ci., 1565), condenses with the sodium compound of ethyl cyanoacetate, yielding the cyano-ester (I.), and that from this ester an almost quantitative yield of the tricarboxylic acid (II.) can be obtained on hydrolysis, has led to an investigation in which the possibility of the existence of "enclosed" or "caged" carbon rings has been studied.



I.

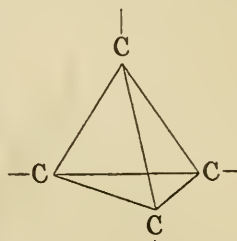
M. p. 30° .



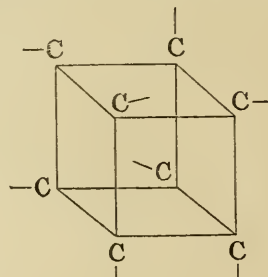
II.

M. p. 172° .

It is evident that the simplest type of such a series would be the enclosed four-carbon ring in which the carbon atoms occupy the four points of a tetrahedron, as in formula (III.), whilst another type would be the "caged" cube as in formula (IV.).



III.

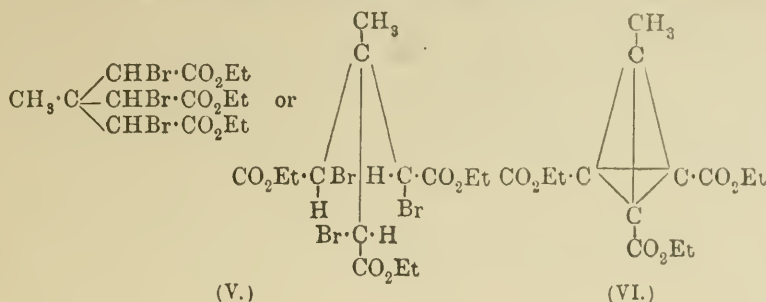


IV.

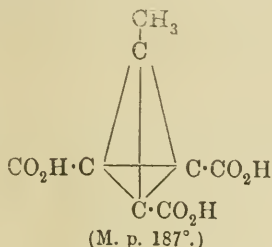
It is well known that the esters of the bromoglutaric acids eliminate hydrogen bromide and pass into derivatives of cyclopropane, and it therefore follows that if this reaction could be applied to the tribromo-ester (V.), which can be prepared by the bromination of the acid (II.), that ring-formation would ensue in accordance with the accompanying scheme (V.) and (VI.).

Many difficulties were experienced in attempting to accomplish this change, because it was found that all the usual reagents, employed for the purpose of eliminating hydrogen bromide, led to the production of the corresponding lactones. Ultimately a reaction was discovered, which has since been found to succeed in a number of other cases, and seems to favour the formation of the carbon ring from compounds of this character. The reaction is carried out by adding the bromo-ester to a very concentrated aqueous solution of potassium hydroxide at 130° . The reaction is very violent, but the more violent it is the better is the yield of the ring compound.

By the aid of this reaction, the tribromo-ester (V.) has been converted into a tricarboxylic acid having the formula



$\text{C}_8\text{H}_6\text{O}_6$, which has all the properties of the "caged" ring tricarboxylic acid:—

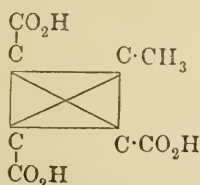


The acid is a remarkably stable substance, and does not decolorise alkaline permanganate in the cold; it is not attacked by bromine at the ordinary temperature. It yields methylsuccinic acid when oxidised by hot alkaline permanganate.

DISCUSSION.

In reply to Prof. Armstrong, Dr. THORPE said that so soon as larger quantities of material had been prepared it was his intention to study the action of hydrogen bromide, but it was necessary in order thoroughly to investigate the products of this reaction that considerable quantities of material should be available.

In reply to Sir W. Ramsay, he said that the formula of the "caged" ring compound could only be expressed in the plane of the paper by:—

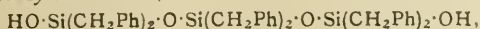


representing the compound as a derivative of cyclobutane, which it certainly was not.

*308. "Organic Derivatives of Silicon. Part XX. Some Condensation Products of Dibenzylsilicanediol." By ROBERT ROBISON and FREDERIC STANLEY KIPPING.

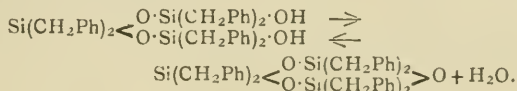
The two condensation products of dibenzylsilicanediol, namely, anhydrosilicanediol and trianhydrosilicanediol (Robison and Kipping, *Trans.*, 1912, ci., 2142), have been further studied in order to ascertain the conditions under which they are formed.

A further condensation product, namely, dianhydrottrisilicanediol,—



has also been obtained by the partial hydrolysis of trianhydrottrisilicanediol with potassium hydroxide, and with hydrochloric acid, in a suitable solvent. This compound crystallises in massive prisms, melting at 82°, and is analogous to dianhydrottrisilicanediol.

silicanediol; it is readily transformed into trianhydrottrisilicanediol when it is treated with hydrogen chloride in alcoholic solution, the following reversible reaction taking place—



*309. "The Rotatory Dispersive Power of Organic Compounds. Part V. A Comparison of the Optical and Magnetic Rotatory Dispersions in some Optically Active Liquids." By THOMAS MARTIN LOWRY, ROBERT HOWSON PICKARD, and JOSEPH KENYON.

After examining thirty-four optically active liquids, only two cases have been found in which the optical and magnetic rotatory dispersions are approximately equal; even this equality is fortuitous, as it does not appear in the next homologues. Wiedemann's law, which applies exactly in the case of quartz, does not therefore hold good for optically active liquids.

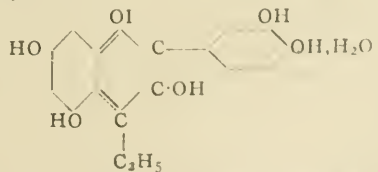
310. "A Relation between Chemical Constitution and Depth of Colour of Dyes." By EDWIN ROY WATSON.

The theory is put forward that those dyes which are quinonoid in all possible tautomeric forms exhibit a deep colour, however simple the molecule may be. On the other hand, if there is the possibility of the molecule existing in a non-quinonoid form, it may not attain a deep colour, although the molecular complexity may be very considerable. A survey of all the better known dye-stuffs fully bears out this theory, and it explains remarkable differences in depths of colour between dyes of very similar constitution. A permanent quinonoid structure alone is not sufficient, for example, dihydroxy-*p*-benzoquinone; the substance must be capable of tautomerising from one quinonoid arrangement to another.

The theory has been fully borne out by the preparation of dyes of deep colour from quercetin.

311. "Dyes Derived from Quercetin." By EDWIN ROY WATSON and KUMUD BEHARI SEN.

By the action of magnesium ethyl iodide on quercetin pentaethyl ether, there is obtained 3:5:7-triethoxy-2-m-*p*-diethoxyphenyl-4-ethyl-1:4-benzopyran anhydrosilicanediol, which, on de-ethylation, yields 3:5:7-trihydroxy-2-m-*p*-dihydroxyphenyl-4-ethyl-1:4-benzopyran anhydrosilicanediol:—



this dyes wool violet (on alum and chrome) and crimson (on tin).

3:5-Dihydroxy-7-keto-4-dimethylaminophenyl-2-m-*p*-dihydroxyphenyl-1:4-benzopyran, obtained from quercetin

by the action of dimethylaniline in the presence of phosphoryl chloride, dyes wool in slaty-blue shades on all mordants. 3 : 4 : 5 : 7-Tetrahydroxy-2-m-p-dihydroxy-phenyl 1 : 4-benzopyran, prepared by the reduction of quercetin by sodium amalgam in alcoholic hydrochloric acid solution, dissolves in alcohol with a magenta colour, and in potassium hydroxide to a green solution, but is very readily oxidised to quercetin.

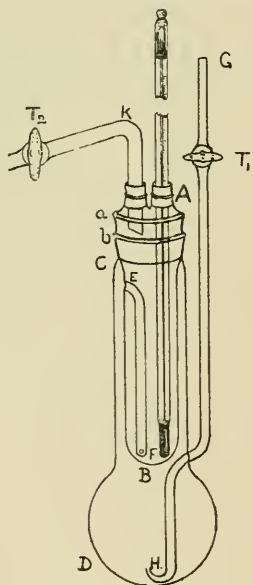
Several other derivatives of quercetin and 2-phenyl-1 : 4-benzopyran were also prepared.

312. "An Improved Apparatus for the Determination of Molecular Weight by the Landsberger-Sakurai Method." By WILLIAM ERNEST STEPHEN TURNER and CORNELIUS THEODORE POLLARD.

The great convenience of the Landsberger-Sakurai method of determining molecular weights, especially as a time-saver (see Note 1), has led to its adoption in principle in a number of pieces of apparatus devised by subsequent investigators. Most of these forms, however, are unsuitable for accurate work, and in a paper which discussed the various sources of error in the Landsberger-Sakurai method (Turner, *Trans.*, 1910, xcvi., 1184) an apparatus was described which enabled rapid and accurate measurements to be undertaken.

During the course of some three years' work with this apparatus, several improvements have suggested themselves, and have been collected in the new form figured below.

The most important alteration of the original is the use of the boiler as the constant temperature jacket (see Note



2). For one of the disadvantages of the Landsberger and Sakurai forms of apparatus is that the molecular-weight tube fills so readily as to make it difficult, with easily condensable vapours, to obtain more than three or four readings in a series. By using the boiler as outer jacket and making the entrance for the vapour stream high up in the molecular-weight tube, the cooler solvent or solution in the tube is heated considerably before the entrance of vapour, and the amount of condensation thus diminished.

The molecular-weight tube AB, 17.5 cm. in length, 2.8 cm. diameter in the main portion, and 3.5 cm. at the mouth, carries a ground-glass stopper with two tubulures, fitting flush with the mouth of the tube at a. To the solvent or solution under measurement, vapour is admitted through two perforations at the bottom of the

tube EF, the entrance E being 12 cm. from the lower end of the molecular-weight tube. The outer jacket CD, of approximately 5 cm. diameter in the cylindrical portion, fits the molecular-weight tube at a second ground joint at b, and carries a safety-tube GH, provided with a tap T₁. Although shown in one piece, the tube sealed into the boiler reached only the level of the tubulated stopper, and the tap was connected by rubber tubing, the ends of the tubes being in contact. Whilst a determination is in progress, T₁ is usually closed in order to drive a steady stream of vapour through E, but when the molecular-weight tube has been removed for weighing, a cork is inserted in the mouth of the boiler, and T₁ is opened to admit dry air, drawn in through drying tubes connected at G. Hygroscopic solvents are thus protected.

Vapour escapes by the tube K, of length as short as possible, connexion with the condenser being made at a third ground joint, so that the molecular-weight tube, together with the thermometer and escape tube, can be lifted away bodily for weighing, during which process the tap T₂ is closed. A small cork may be inserted at E if desirable, and complete protection from moist air thus secured.

Of other points it may be remarked that the molecular-weight tube is graduated with marks 2 mm. apart to assist in determining the correction for the use of boiling-point due to increasing head of liquid (alternatively the graduation may be in cc.); that the thermometer used is one of the Beckmann type specially made by Baumbach, of Manchester; and that it is advantageous to protect the cylindrical portion of the outer jacket by two or three thicknesses of asbestos paper, and so diminish the loss of heat by radiation.

The following results were obtained during the course of little more than an hour from the time of setting up the apparatus:—

Pyrogallol in Ethyl Alcohol. $C_6H_3(OH)_3 = 126.0$.
(Weight of Solute, 0.8090 grm.).

Weight of solvent. Grms.	Δ°	M.W.
9.69	0.773	124.9
11.90	0.625	125.7
14.31	0.530	123.7
16.71	0.444	126.1
19.17	0.399	124.0
21.92	0.332	128.3
23.96	0.277	128.4

Mean 125.9

Several readings did not mark the limit of the capabilities of the apparatus with this solvent, and as no more than five could, as a rule, be obtained with the earlier form, the efficiency of the new apparatus is considerably greater. Ethyl ether, carbon disulphide, and water are easier to handle than alcohol, and with them quite a long series of readings is obtainable. When, however, the boiling point of the solvent exceeds 100°, the number of readings becomes less, so that with amyl alcohol, for example, only four readings were obtained. Above 150° the apparatus may conveniently be employed only in measurements where it is sufficiently accurate to assume that the volume of the solution is the volume of the solvent; for in such a case it is unnecessary to detach the molecular-weight tube, thus avoiding the inconvenience of handling it at a high temperature.

For a discussion of the details requiring attention and the corrections to be applied in accurate work, reference should be made to the previous paper on the subject.

Note 1.—Besides saving time, the rapidity of the process permits the investigation of substances which would decompose during the prolonged boiling involved in the ordinary Beckmann method. Such substances are triethylsulphonium salts (see Turner, *Trans.*, 1911, xcix., 880) and amylamine hydrochloride (Turner, *loc. cit.*; compare Hantzsch and Hofmann, *Ber.*, 1911, xlv., 1776).

Note 2.—In much the same way as used by McCoy (*Amer. Chem. Journ.*, 1900, xxiii., 353) and Ludlam (*Trans.*, 1902, lxxxi., 1193).

(We are indebted to the Chemical Society for permission to reproduce the accompanying woodcut.)

(To be continued).

SOCIETY OF CHEMICAL INDUSTRY.
(LONDON SECTION).

Ordinary Meeting, January 5th, 1914.

Dr. W. R. E. HODGKINSON in the Chair.

The following papers were read and discussed:—

"Viscosity of Oils." By J. L. STREVEIS.

The author, after emphasising the importance of the determination of absolute viscosity and its relation to temperature for any particular lubricant, proceeds to correct certain figures previously published by Dunstan and himself on the basis of the more correct case for the viscosity of phenol at various temperatures due to Dunstan and Thole.

1. Increase of molecular weight favours increase of Z_t , e.g., rape oil (trienium) $>$ olive oil (triolein).

2. Hydroxyl formation favours increased Z_t , e.g., castor oils and the blown oils.

3. Solution of solid bodies in oils (e.g., "soaping") tends to a high viscosity temperature coefficient.

4. Combined high molecular weight and conjugated double bonds mean a high Z_t , e.g., tung oil.

5. Unsaturation tends to lower the viscosity, and broadly the greater the iodine value the lower Z_t , e.g., linseed and perilla oils less than nut or olive oil.

Experimental results are given and the recent work of Higgins at the National Physical Laboratory is referred to.

"Oxygen Content of the Gases from Roasting Pyrites." By LEWIS T. WRIGHT.

The author calls attention to the discussion that arose forty years ago between Scheurer-Kestner and Friedr. Bode on the deficiency noted by the former in the oxygen of the gases from roasting pyrites if the pyrites were fully oxidised according to the equation $2FeS_2 + 11O = Fe_2O_3 + 4SO_2$.

The matter was not satisfactorily cleared up by this discussion in which Lunge took part, because the amount of SO_3 formed either free or as metallic sulphate in the cinder did not explain the full extent of the deficiency. Lunge suggested there might also be some error in the absorption of the oxygen by the pyrogallate in the course of the gas analysis. The author, on examining a number of analyses of "burner" gas from various sources, noticed that the oxygen "deficiency" is the greater the greater dilution of the gas, and this suggests that there is, in addition to the well-known production of SO_3 and metallic sulphates, some other cause, such as a constant error in the analyses which influences these. In any case the evidence of these gas analyses shows that the manner in which the oxygen is disposed of would prevent the "burner" gas from containing more than about 12 per cent of SO_2 as a maximum when all the oxygen of the air applied was used up, and the author states that his various attempts to obtain more than this in practice by keeping burner gas long in contact with incandescent pyrites have failed.

"Electrical Conductivity of Milk during the Concentration, with Suggestions for a Practical Method of Determining the End-point in the Manufacture of Sweetened Condensed Milk." By L. C. JACKSON, LESLIE MCNAB, and A. C. H. ROTHERA.

The authors have studied the variation of the electrical conductivity of milk during the process of concentration. They find that although the measurement of electrical conductivity is of no value in determining the degree of concentration of a separated unsweetened milk, it can

be made the basis of a working process for watching the concentration of sweetened whole milk.

An ingenious device in which the resistance of sweetened milk in the vacuum pan is compared with that of an approved sample of condensed milk maintained at exactly the same temperature is described.

Numerous experiments on which the authors base their method are described in the paper.

"Monazite from some New Localities." By SYDNEY J. JOHNSTONE.

In this paper are given the results obtained and the methods of analysis employed in the examination of twenty-one samples of pure monazite from new localities in Ceylon, Travancore, Nyassaland, Malaya, Northern and Southern Nigeria. The results show that wide variation may occur in the quantity of thorium present in samples; notable amongst these are ranges shown by those from Ceylon whose thorium percentage varies from 9.5 to 28.2, from Malaya 3.4 to 9.4, and from Northern Nigeria 2.3 to 8.0.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 20, November 17, 1913.

Thermochemistry of Acetylenic Compounds.—Charles Moureu and Enile André.—The heat of hydrogenation of acetylenic compounds is considerable. It is of the order of 80 cal. in the fatty series and decidedly less in the aromatic series. The fixation of the first half of the hydrogen (2 atoms) to give an ethylenic compound generally liberates more than half of the heat disengaged in the complete saturation. The excess of energy of the triple bond over the simple bond is about 70 cal. in the first members of the series. The fixation of water by an acetylenic hydrocarbon, with formation of a ketone, liberates a quantity of heat of the order of 40 cal.

Influence of Silicon on the Solubility of Carbon in Iron.—Georges Charpy and André Cornu.—Silicon gradually diminishes the solubility of carbon in iron until it becomes practically equal to zero at 900°, when the amount of silicon present exceeds 4 per cent. It also vanishes at 1000°, when the percentage of silicon exceeds 7.

Complex Salts of Uranium.—Paul Pascal.—When uranyl pyrophosphate is dissolved in a solution of the sodium salt the solidification point rises, reaches a maximum, when the two salts are present in the proportion $3P_2O_7Na_4 : P_2O_7(UO_2)_2$, and then descends to a minimum at $2P_2O_7Na_4 : P_2O_7(UO_2)_2$. Up to this point the solution exhibits none of the properties of uranyl salts. When the solution is saturated with uranyl pyrophosphate the ratio is $P_2O_8Na_4 : P_2O_7(UO_2)_2$, and the liquid then exhibits the properties of a strongly diluted uranyl salt. The intermediate pyrophosphate must be regarded as a normal uranyl pyrophosphate of formula $(UO_2)_2(P_2O_7)_4Na_8$. The evaporation of its solution gives a gummy mass which treatment with methyl alcohol transforms into a hygroscopic powder, $[(UO_2)_2(P_2O_7)_3]Na_8 \cdot 6H_2O$ at 15° (+4H₂O at 100°). The saturated solution of uranyl pyrophosphate contains the uranyl sodium salt of the acid. It is a yellow unstable powder, readily transformed into the isomeric double pyrophosphate $P_2O_7(UO)_2Na_2 \cdot H_2O$. All these complex salts are dissociated when their solutions are heated. Alcoholic solutions of potassium cyanate and uranyl nitrate when mixed give a yellow microcrystalline precipitate of formula $[UO_2(CNO)_4]K_2$. This complex salt is analogous to the anhydrous cobaltocyanate, $Co(CNO)_4K_2$. In water it gradually dissociates, giving an orange double salt, $2UO_2(CNO)_2 + KCNO$. An excess of alkaline cyanate causes the formation of the salt $UO_2(CNO)_2 + KCNO$, while

an excess of uranyl salt precipitates $\text{UO}_2(\text{CNO})_2$. These two examples are not isolated, and according to the acid radicle introduced the uranyl complex can have either of the following constitutions: $[\text{UO}_2\text{X}_6]\text{M}_4$ or $[\text{UO}_2\text{X}_4]\text{M}_2$. The first type is always very stable; it resists hydrolysis and the uranium reactions are completely masked in it. The second type in dilute solution behaves like a double salt, and an enormous excess of alkaline salt is necessary to prevent dissociation.

Action of Carbon Dioxide on Boron Sulphide.—N. D. Costeanu.—Carbon dioxide acts on boron sulphide in the same way as on silicon sulphide, transforming it into boric anhydride with formation of carbon monoxide and sulphur: $\text{B}_2\text{S}_3 + 3\text{CO}_2 = \text{B}_2\text{O}_3 + 3\text{CO} + 3\text{S}$. The reaction begins at 300° , but the change is not rapid at this temperature. It is accelerated by raising the temperature and prolonging the heating, but it never occurs very quickly owing to the formation of a protective layer of B_2O_3 on the surface of the sulphide.

Colours of Glasses containing Copper.—Albert Granger.—Glasses are coloured blue by copper when only a very small amount is present. With 0.05 CuO for a molecule of base a very satisfactory blue coloration is obtained. On increasing the amount of copper the glass shows a tendency to turn green, and this tendency is increased by the addition of alumina or boric anhydride. Glasses containing boric anhydride have a very dark colour; when they are some millimetres thick they are nearly opaque. The most important factor in the preparation of a blue glass is a convenient proportion between the bases; the acidity of the glass has no effect on the tint. Certain glasses show a tendency to deposit copper when they are quickly cooled.

Products of Concentration of Nitrated Benzyl Chlorides with Acetylacetone, Methylacetylacetone, and Cyanacetic Ethers.—H. Mech.—When di-*p*-nitrobenzylacetylacetone is reduced with zinc and hydrochloric acid the product is di-*p*-aminobenzylacetylacetone. *p*-Nitrobenzyl chloride reacts with methylacetylacetone to give methyl-*p*-nitrophenylbutanone. Di-*p*-nitrobenzylcyanacetate of methyl is readily obtained by the action of nitrated chlorides of benzyl upon a solution in methyl alcohol of sodium methyl cyanacetate.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, January 20, at 3 o'clock, Prof. W. Bateson will deliver the first of a course of six lectures at the Royal Institution on "Animals and Plants under Domestication"; on Thursday, Jan. 22, Mr. W. McDougall, M.A., F.R.S., begins a course of two lectures on "The Mind of Savage Man"; and on Saturday, Jan. 24, Prof. Frederick Corder will give the first of three lectures, with musical illustrations, on "Neglected Musical Composers—(1) Ludwig Spohr, (2) Henry Bishop, (3) Joachim Raff." The Friday Evening Discourse on January 23 will be delivered by Prof. Sir James Dewar, on "The Coming of Age of the Vacuum Flask"; and on Jan. 30, by Mr. H. Wickham Steed, on "The Foundations of Diplomacy."

Mining Exhibition.—The Third Annual Mining Exhibition under the auspices of the Chemical, Metallurgical, and Mining Society of South Africa, will be held in the Volunteer Drill Hall, Twist Street, Johannesburg. The Exhibition will open on Tuesday, May 19, and will close on Friday, May 29, 1914. The scope of the Exhibition will be on much the same lines as in previous years, *i.e.*, chemical, metallurgical, and mining apparatus and device for laboratories, works, and mines; models, working or otherwise, of apparatus for similar purposes; plans, diagrams, &c., of mines, works, plants, machinery, and apparatus; safety and rescue and other ambulance apparatus and appliances; and specimens of crude and manufactured mineral or other natural products of South Africa. The

Exhibition is primarily for the benefit and information of those engaged and interested in mining work, and to give those in search of mineral products an opportunity of ascertaining where these products may be obtained. Commercial firms, for whom a limited space will be provided, desirous of exhibiting machinery, apparatus, natural products, &c., will be charged for the space occupied at from 5s. to 10s. per square foot, according to position, and whether stands are provided or not. Those desirous of engaging space provisionally are requested to specify their requirements with the least possible delay to the undersigned. The usual arrangements for exhibitions with regard to Customs duties and railway rates will be made. —FRED ROWLAND, Secretary, South African School of Mines and Technology Building, Eloff Street, Johannesburg.

MEETINGS FOR THE WEEK.

- MONDAY, 19th.—Royal Society of Arts, 8. (Cantor Lecture). "The Relation of Industry to Art," by Sir Charles Waldstein, Litt D., Ph.D.
- TUESDAY, 20th.—Royal Institution, 3. "Animals and Plants under Domestication," by Prof. W. Bateson, F.R.S., &c.
- WEDNESDAY, 21st.—Royal Society of Arts, 8. "The Modern Poster, its Essentials and Significance," by W. S. Rogers.
- Microscopical, 8. Presidential Address by Prof. G. Sims Woodhead, "The Microscope and Medicine."
- THURSDAY, 22nd.—Royal Institution, 3. "The Mind of Savage Man," by W. McDougall, F.R.S.
- Royal Society. "Heat Production Associated with Muscular Work" (a Note on Prof. Macdonald's Paper, *Proc. R. S.*, B, lxxxvii.), by R. T. Glazebrook and D. W. Dye. "Chemical Interpretation of some Mendelian Factors for Flower Colour," by M. Wheldale and H. L. Bassett. "Determination of the Minimum Letal Dose of various Toxic Substances and its Relationship to the Body Weight in Warm-blooded Animals, together with considerations bearing on the Dosage of Drugs" by G. Dreyer and E. W. A. Walker. "Experiments on the Restoration of Paralysed Muscles by means of Nerve Anastomosis—Part II., Anastomosis of the Nerve supplying Limb Muscles," by R. Kennedy. "Variations in the Sex Ratio of *Mus rattus* following an Unusual Mortality of Adult Females, based on an Analysis of Weight Frequency Distributions," by F. N. White.
- Chemical, 8.30. "Crystals of Organic Compounds Coloured Blue by Iodine," by G. Barger and W. W. Starling. "Preparation and Properties of Pure Formic Acid" and "Mutual Solubility of Formic Acid and Benzene and the System Benzene—Formic Acid—Water," by A. J. Ewins. "Loose Compounds of Cholesterol with Barium Methoxide," by E. Ewbery. "Vapour Pressure of Nitrogen Peroxide," by A. C. G. Egerton. "Organic Derivatives of Silicon—Part XXII., The Siliconic Acids," by C. J. Meads and F. S. Kipping. "Condensation of Glutaconic Ester," by R. Curtis and J. Kenner. " β -Hydrindamine," by J. Kenner and A. M. Mathews. "Reactions of Isoamarine, with Notes on *d*- and *iso*amarine Sulphates and Amended Values of the Rotatory Power of *d*- and *iso*amarine," by H. L. Snape. "Constituents of *S. lunum angustifolium*" and "Solangustine, a New Gluco-alkaloid," by F. Tutin and H. W. B. Clewer. "Studies of the Constitution of Soap Solutions—the Electrical Conductivity of Potassium Salts of Fatty Acids," by H. M. Bunbury and H. E. Martin. "Occurrence of three Partially Miscible Liquids in a Four-component System, Ether—Water—Potassium Iodide—Mercuric Iodide, at 20° ," by A. C. Dunningham. "Inversion of Cane-sugar by Acids in Water-Alcohol Solutions," by C. J. Burrows.
- FRIDAY, 23rd.—Royal Institution, 3. "The Coming of Age of the Vacuum Flask," by Prof. Sir James Dewar, F.R.S., &c.
- Physical, 5. "Some Characteristic Curves and Sensitiveness Tests of Crystal and other Detectors," by P. R. Coursey. Exhibition of Water Model of the Musical Arc, by W. Duddell. "Experiments with Liquid Drops and Globules" by C. R. Darling. Note on Aberration in a Dispersive Medium and Airy's Experiment," by J. Walker.
- SATURDAY, 24th.—Royal Institution, 3. "Neglected Musical Composers," by Prof. F. Corder.

THE CHEMICAL NEWS.

VOL. CIX., No. 2826.

THE ESTIMATION OF ALCOHOL IN BEER BY MEANS OF MALLIGAND'S EBULLIOSCOPE.

By JOHN CANNELL CAIN.

IN view of the fact that the methods usually employed for the estimation of alcohol in beer involve the use of more or less complicated chemical apparatus, including often a delicate balance, and the employment of gas and water, it is rather remarkable that determinations with the simple apparatus invented by Vidal and improved by Malligand and Mlle. E. Brossard-Vidal (*Comptes Rendus*, 1874, lxxviii., 1470) seem hitherto not to have been published in this country.

This is the more surprising as it has been abundantly proved that the apparatus furnishes very exact results, and it combines the great advantage that a determination can be carried out in a few minutes, and no chemical appliances are required for its use. Thus Dumas, Desain, and Thenard (*Comptes Rendus*, 1875, lxxx., 1114) presented a report to the French Academy in which they showed that by means of the ebullioscope the estimation of alcohol in wine could be carried out with great exactness, and Griessmayer (*Dingler's Polytech. Journ.*, 1875, ccxviii., 262) proved the same in the case of German beers. Further, in a long report to the Royal Finance Department, Kristiania, Waage ("Ebullioskopet og dets Anvendelse ved Beskatning af Oliefter dets Alkoholgehalt"; see also *Zeit. Anal. Chem.*, 1879, xviii., 417) made an exhaustive examination of this method, and demonstrated that it yielded accurate results, which he illustrated by comparative analyses of a large number of Scandinavian beers.

It therefore appeared to be of interest to apply this method of estimating alcohol to the case of English beers, and the results confirm those of the authors already mentioned in that the method is shown to be exact, rapid, and capable of being used by anyone who can read a thermometer.

The principle of the method depends of course on the fact that the boiling-point of an alcoholic liquid is lower than that of water in proportion to its alcohol content, and it has been proved by the above investigators that the solids present in beers and wines exert no practical influence on the boiling-point as their molecular weights are so great.

In making an experiment distilled water is first placed in the lower part of the vessel (up to the mark inside), the lid screwed on, the thermometer (graduated in figures showing directly the alcohol-content in volume per cent) inserted in place, the condenser filled with cold water and screwed into the corresponding opening in the lid, and the water heated to boiling by means of the spirit-lamp, which should be shaded by cardboard to prevent draughts. When the water has boiled steadily for a short time the mercury thread of the thermometer (which will have moved gradually along the tube) remains at one point, and the scale of the thermometer is moved by means of the controlling screw until the zero point is coincident with the position of the end of the mercury thread. The water may be boiled until steam begins to escape through the condenser, by which time the zero point will have been accurately ascertained. This determination is required on each day that the instrument is to be used, as this renders any other correction for barometric pressure unnecessary.

After having fixed the zero point the estimation of alcohol in beer may be made. The beer (at any tempera-

ture) is filled up to the mark and boiled as described in the case of water. It has been found convenient to take readings at intervals of fifteen seconds, beginning when the regular boiling commences. The true boiling-point is not reached until the beer has been boiling steadily (easily recognised by placing the ear near the top of the condenser, when a continuous bubbling is heard) for some time, when the mercury remains stationary. By this time the condenser will have become hot, and if the boiling be continued the mercury advances again and vapour escapes from the top of the condenser. The following readings, taken at fifteen seconds interval, are quoted in order to show the course of the experiment.

6.4	5.8	} True boiling point.
6.1	5.8	
6.05	5.8	
6.05	5.8	
5.95	5.7	} Alcohol escaping.
5.9	5.6	
5.85	5.65	
	5.6	

A determination by the distillation method gave 5.8 per cent. In order to prove the accuracy of the method in the case of English beers, estimations were made of the alcohol-content of a number of various samples purchased at random. The alcohol was determined first by the ebullioscope and secondly by the distillation method. It will be seen that the agreement is quite satisfactory. The alcohol-content is given in volume per cent (cc. of absolute alcohol per 100 cc. of beer; the weight percentage could of course be obtained by a determination of the specific gravity of the beer and a simple calculation).

Bottled Beers.

	Ebullioscope.	Distillation.
Mann, Crossman, and Paulin's "family ale"	4.75	4.65
Mann, Crossman, and Paulin's "brown ale"	5.0	5.0
Mann, Crossman, and Paulin's "dinner ale"	5.0	4.9
Whitbread and Co.'s "family ale"	5.8	6.0
Whitbread and Co.'s "dinner ale"	5.65	5.75
Meux's "light pale ale"	5.3	5.2
Benskin's "bitter pale"	5.05	4.95
Truman, Hanbury, Buxton, and Co. Ltd., "family ale"	3.75	3.85
Bass's "East India pale ale"	6.3	6.3
Worthington's "India pale ale"	6.9	7.1
Ind, Coope, and Co.'s "Romford ale"	5.5	5.3
Allsopp's "light dinner ale"	5.9 5.8	5.85
Allsopp's "India pale ale"	6.25	6.15
Marston, Thomson, and Evershed's, Ltd., "pale ale"	6.3	6.35
Reid's "family stout"	5.3	5.0

Draught Beers.

Whitbread's "KK Burton pale"	8.8	8.8
Benskin's "India pale ale"	6.2	6.2
Whitbread's "light bitter ale"	5.8	5.8
Whitbread's "mild ale"	6.05	6.15

Lager Beers.

Allsopp's "Lager"	4.6	4.5
Imported German "Pilsener"	4.7	4.8
Imported German "Munich"	4.3	4.2

My thanks are due to Sir William Ramsay, K.C.B., for suggesting this work, and for affording me facilities for carrying it out at University College.

AN ACCURATE METHOD OF ANALYSIS OF ALUMINIUM.

By HARI PADA BHATTACHARYYA, M.A.

Total Silicon.—Weigh 1 grm. in a porcelain basin, and add to it 20 cc. strong HNO_3 (sp. gr. 1.45), and keep it covered on the hottest part of a hot plate. The metal will dissolve with evolution of nitrous fumes. The cover is then removed, and the solution is allowed to evaporate down to dryness. The basin is taken away from heat and allowed to cool. When cool, 15 cc. of HCl is added and the solution is evaporated down and baked, and again dissolved in 15 cc. HCl . When the solution becomes clear, 15 cc. of water is added. This is now boiled and taken away to cool, and then filtered through Swedish filter-paper and washed with warm hydrochloric acid and cold water, and afterwards with hot water till the last trace of acid is removed. The residue is ignited wet in a silica crucible and weighed. It is then treated with HF and H_2SO_4 in the usual way.

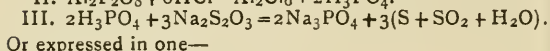
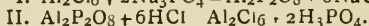
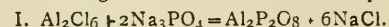
(N.B.—15 cc. HCl and 5 cc. H_2SO_4 were also tried; the result was not different).

Iron.—Dissolve in a beaker 1 grm. of drillings in 30 cc. of a 25 per cent solution of chemically pure NaOH . As soon as the solution is clear filter it and wash with hot water till the last trace of alkali is removed. Dissolve the residue in warm HCl (1:1), and wash the filter-paper with hot water.

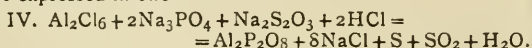
Precipitate Fe with ammonia and estimate gravimetrically. (When there is much copper it requires to be dissolved in dilute HNO_3 warm and added to the HCl solution, then precipitate Fe with HN_4HO ; Cu will show blue filtrate).

Copper.—Pass SH_2 through the filtrate from SiO_2 , and estimate Cu as CuO .

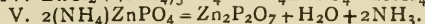
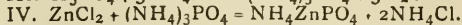
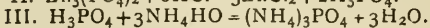
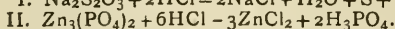
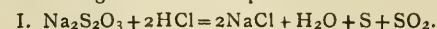
Aluminium.—The filtrate, after the removal of the copper sulphide as above, is boiled to remove SH_2 , and then diluted to make up 1 litre, 100 cc. of which is taken for estimation of aluminium. Add 1 grm. Na_3PO_4 ; dilute to about 200 cc., neutralise with ammonia to precipitation, and just re-dissolve with a drop or two of HCl . Boil and add sodium thiosulphate solution in excess. (N.B.—It thiosulphate is added to the cold solution it bumps violently when boiling). Boil till the smell of SO_2 is no longer perceived, and then allow to settle. Filter and wash with boiling water till the washings are free from alkaline phosphate (to be tested with AgNO_3 solution). The precipitate filters and washes quickly. Ignite in a silica crucible, and weigh as AlPO_4 . (Factor 22.22 per cent Al). The following are the reactions that take place:—



Or expressed in one—



Zinc.—The filtrate from the precipitation of Al is made ammoniacal and boiled till the solution shows amphoteric reaction to litmus-paper. Filter and wash with boiling water. Ignite and weigh as $\text{Zn}_2\text{P}_2\text{O}_7$ ($\text{Zn} = 42.91$ per cent). The following reactions take place:—



Sodium.—This is estimated by the usual method, viz., solution in strong nitric acid (1.45 sp. gr.) is evaporated to dryness and baked; 5 cc. HNO_3 is added again, and again dried and baked, then ignited to drive off nitrous fumes, cooled, and crushed to powder; added boiling water, boiled, the clear liquid decanted, and the residue washed with boiling water. The whole is evaporated

down to dryness. Dissolve the residue in 25 cc. hot water, and add a drop of NH_4HO to see if there is any Al present. Convert to chloride and weigh, &c.

The following experiments may prove of interest:—

1. 0.1 grm. aluminium (99 per cent purity) and 0.1 grm. Zn (99.95 per cent purity) were weighed in a beaker and dissolved in HCl , and aluminium was separated, washed, dried, and ignited; from the filtrate Zn was estimated as pyrophosphate. The following figures were obtained:— $\text{Al} = 0.099$ grm.; $\text{Zn} = 0.09995$ grm.

2. 0.1 grm. aluminium (99 per cent purity) was weighed in a beaker and dissolved in HCl , and Al was estimated by the method. 0.099 grm. was the figure obtained. The filtrate was free from aluminium.

3. 0.1 grm. zinc was weighed in a beaker and dissolved in HCl . The excess acid was boiled out, diluted, added sodium phosphate, the precipitate cleared with HCl , boiled, and added hypo solution, boiled, filtered, and washed. The filter-paper is ignited and weighed.

Ash.—0.00056 obtained, which was the ash of 11 cm. Swedish filter-paper, showing that Al precipitate is not contaminated with Zn .

The filtrate is treated for Zn . Zn weighed 0.09995 grm.

The above experiments show the accuracy of the method.

Carbon.—This has been determined by the sodio-copper chloride process. But this reagent must be added gradually drop by drop over water (25 cc.) in which the aluminium drillings are placed, otherwise a too violent action will take place and some C will be lost. Filter the carbon through asbestos, and estimate it by a wet combustion as usual.

Gun and Shell Factory, Ishapore, Bengal.

PASSIVITY.*

By GERHARD C. SCHMIDT.

1. Introduction.

ALTHOUGH the abnormal chemical and electrochemical behaviour of iron and certain other metals has been known for more than 100 years, up to the present no explanation of the cause of passivity has met with general acceptance. In course of time many theories have been suggested and subsequently given up. At the present time only two theories deserve serious consideration: (a) the oxide theory of Faraday, according to which passivity is due to a coating of oxide or oxygen on the metal—a theory which still finds supporters in spite of the many serious objections put forward against it—and the hydrogen theory, according to which the metals in question are normally passive and become active only in the presence of dissolved hydrogen acting as a catalyst. The latter view has recently been strongly supported by my pupils, Grave (*Zeit. Phys. Chem.*, 1911, lxxvii., 513) and Adler (*Ibid.*, 1912, lxxx., 385), on the basis of experimental investigations. Flade ("Habilitationsschrift," Marburg, 1910; *Zeit. Elektrochem.*, 1912, xvii., 335) does not regard their results as conclusive, and considers that his own investigations lend support to the oxide theory. In the present Paper the results of further experiments designed to decide between these two theories are described.

2. Criticism of Flade's Results.

Flade found that iron rendered passive by anodic polarisation in dilute sulphuric acid immediately returns to the active state when the polarising e.m.f. is removed.

When, however, it is in a circuit and forms the anode under the influence of an external, not too great, e.m.f., the potential gradually becomes more negative, until at a certain potential, the "transition point," it suddenly

* A Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, November 12, 1913. (Experimental Part by W. RATHERT.)

becomes active. Flade regards this point as the long sought limit between the active and passive states.

The arrangement used by Flade is practically identical with that of Fredenhagen (*Zeit. Phys. Chem.*, 1908, lxiii., 1), and the question arises whether the transition point discovered by Flade is not the "activation potential" of Fredenhagen. If this should prove to be the case it follows, since Fredenhagen has shown that the "activation potential" and the "passivation potential" are quite different, that the formation of well-defined oxides is excluded. This point was first investigated.

3. Experimental Results.

As a result of investigations which will be fully described elsewhere, it was found that the "transition point" is in fact identical with the activation potential of Fredenhagen, and, further, that in all cases the activation potential and the passivation potential are different. The transition point does not form a boundary between the active and the passive states, since iron can remain active at a potential which is much more positive (more noble) and passive at a potential much more negative than that corresponding with the transition point. Further, experiments with wires of different lengths show that the transition point has not always the same value. In fact, the determining factor in these investigations is the current density, or in other words the amount of oxygen set free by the current. The investigations of Flade furnish evidence against the oxide theory, since, as Fredenhagen has pointed out, the activation and passivation potentials must coincide if oxides are formed. On the other hand, the results in question can readily be accounted for on the basis of the hydrogen theory. When iron is rendered passive by anodic polarisation, the oxygen combines with the hydrogen diffusing through the iron towards the surface and thus retards solution of the metal. The iron remains passive as long as the oxygen is being liberated freely. As the amount of oxygen liberated falls off with diminishing current density a point is reached when it is no longer sufficient to combine with all the hydrogen. The iron becomes active at one point; hydrogen is immediately set free at this point, neighbouring regions become active as a consequence of local currents, and thus the whole surface becomes active with explosive rapidity. When the attempt is now made to reverse the condition of the metal, considerable resistance is met with on account of the considerable content of hydrogen and its high absorptive power for this gas. As the rate of liberation of oxygen increases, the potential gradually becomes more positive (nobler), the metal becoming passive at certain points: at other points solution of the metal proceeds and the evolved hydrogen tends to remove the passivity. As the current density and the consequent liberation of oxygen are further increased, more and more of the metal is rendered passive, until a point is ultimately reached at which the tendency to activity is overcome and the whole of the metal becomes passive. This change cannot proceed with the same rapidity as the converse one, on account of the strongly marked tendency of iron to remain active, and it is therefore not to be anticipated that the activation and passivation potential will coincide—a conclusion fully confirmed by experiment.

The behaviour of chromium is the converse of that of iron, the active condition in this case being the normal. Corresponding with this the transition point with evolution of hydrogen is quite sharp.

4. The Effect of Polishing.

Although the results of Flade and those subsequently obtained in the Münster laboratory can be explained on the hydrogen theory, they do not constitute a conclusive proof of the validity of that theory. The results described below allow, in my opinion, of a definite decision between the two theories.

The guiding principle in these investigations is as follows: According to Muthmann and Frauenberger

(*Sitzungsber. Kgl. Bayr. Akad.*, 1904, xxiv., 201) passivity is brought about by the presence of oxygen dissolved in the metal. Flade accepts this view only as regards the action of air in causing passivity; all other passivity phenomena are ascribed to the formation of oxide films on the metal. On either of these assumptions any metal the surface of which is cleaned in the entire absence of oxygen must be active, whilst according to the hydrogen theory it is to be anticipated that iron, which always contains hydrogen, would be active, and chromium and nickel, which do not contain hydrogen, would become passive.

In order to test these conclusions an apparatus was constructed in which the metals could be subjected to friction in an atmosphere of hydrogen or nitrogen and the potentials then determined at once. The gases were very carefully purified and air was completely excluded. It was found that when subjected to friction in hydrogen, chromium and nickel became rather more positive (nobler) but remained completely passive. These results show conclusively that metals may remain passive in the absence of oxygen, under circumstances in which the formation of an oxide film is impossible—results which cannot be reconciled with the oxide theory. The small differences of potential observed when metals are subjected to friction in different gases are due to adhering layers of gas. Iron, on the other hand, was always found to be active even in neutral solutions of ferrous sulphate: it is naturally a less noble metal than chromium or nickel, and, as the investigations of Belloc (*Ann. Chim. Phys.*, 1909, xviii.) and others have shown, always contains considerable amounts of hydrogen.

5. Effect of a Hydrogen Charge on the Potential and Activity of a Metal.

In the foregoing sections it has been proved that metals which contain no alloy with oxygen and are free from coatings of oxide can retain the passive condition, but in order to show the validity of the hydrogen theory it is further necessary to prove that dissolved hydrogen can transform metals from the passive to the active form. For this purpose metals prepared by electrolytic methods and therefore containing hydrogen were examined; and, further, hydrogen was liberated at a point and conveyed by diffusion to other passive portions of the surface, under which circumstances the passive portions regained their activity.

As already mentioned, ordinary iron is active in ferrous sulphate solution, probably owing to the large proportion of hydrogen it contains. Electrolytic iron is also active under these conditions, showing a less noble potential than ordinary iron. The potential $e_h = -0.66$ volt found by Muthmann and Frauenberger (*loc. cit.*), is, as shown by Richards and Behr, too high; it represents the potential of iron supersaturated with hydrogen. The value $e_h = -0.423$ volt obtained by us in good agreement with that given by Richards and Behr, is also that of a metal containing hydrogen. Muthmann and Frauenberger found that the potential can be made more negative (less noble) by adding more hydrogen, and it seems plausible to assume that by the withdrawal of hydrogen the potential will become more positive, and that finally the metal will become passive. These conclusions cannot be satisfactorily tested experimentally, as the amount of hydrogen in iron in any given case is not known and the gas cannot be completely removed from the metal.

The matter can, however, be tested in the case of nickel and of chromium. Ordinary nickel in nickel sulphate and chromium in dilute sulphuric acid are completely passive. On the other hand, electrolytic nickel and chromium, which are both highly charged with hydrogen, are active and go into solution with evolution of hydrogen. (According to Carveth and Curry, *Journ. Phys. Chem.*, 1905, ix., 353, electrolytic chromium contains 250 times its volume of hydrogen). If chromium is deposited

electrolytically on a sample of the same metal prepared by the Goldschmidt process, and which is quite inactive, the latter under the influence of the hydrogen also dissolves in dilute sulphuric acid. His results are in entire agreement with those of Hittorf, who showed that even the minute trace of hydrogen liberated at a chromium electrode by making it a cathode for a moment renders the metal active. In my investigations just described the hydrogen which starts the reaction is contained in the electrolytic iron. The phenomena just described, at least as far as chromium and nickel are concerned, must be regarded as "experimenta crucis" in favour of the hydrogen theory. When the metals are prepared electrolytically or by reduction at a high temperature and subsequent rubbing in an atmosphere of hydrogen, they differ only in electrochemical behaviour and in the extent to which they are charged with hydrogen. The assumption that these two factors are in casual connection cannot be avoided, especially as the possibility of the formation of oxides or alloys with oxygen is excluded.

The experiments with iron are, however, not decisive, since it always remained active. The following investigations supply the evidence required.

(To be continued).

THE MANUFACTURE OF HYDROGEN FOR BALLOONS. PORTABLE PLANTS FOR MILITARY USE.

THE progress recently made in developing balloons and airships for military and other uses has caused increased attention to be paid to methods for producing hydrogen gas in large quantities and in a sufficiently pure state. Of late the extensive use of airships in some countries as a part of the army outfit has led to a search for suitable hydrogen-producing plants especially adapted for military use. Fixed hydrogen plants are of course useful in connection with aeronautic establishments and army centres, but what is especially valuable now is a portable outfit; by the adoption of a hydrogen plant mounted upon railroad cars it will be seen that the effective work of an airship will be at once increased. Similarly the gas from such a movable plant can be used in different industries developed within the last few years, such as electric welding of plates or bars, and similar work, for which a considerable amount of hydrogen is needed at present, also for cutting plate iron by the hydrogen blowpipe.

The hydrogen-producing methods used mainly up to now are purely chemical, electrolytic, or regeneration processes, but all have their disadvantages as compared with the oil-gas method. In some cases the first cost or operative expenses are high, and in others the gas needs to be produced on the spot where hydraulic or other cheap electric power can be employed, or in other cases where a water-gas plant can be installed to advantage. Some processes do not give a pure enough hydrogen; for example, the gas for use in airships must be free from chlorine, for chlorine attacks the balloon envelope.

According to the new German hydrogen process devised by Rincker and Wolter, the gas can be produced in any suitable place, and the plant occupies but a small space, with a very cheap production. At the same time the compact shape of the apparatus makes it very well adapted for mounting upon cars so as to give a portable plant for airships. The gas which is produced in this apparatus has only a small percentage of nitrogen and has a specific gravity of 0.087 to 0.092. The operation is based upon the use of crude oil to produce the gas, or the producer can be made to work on benzene, refined oil, benzoyl, and the like. Heating is done by the use of coke as a general rule, although this can be replaced by charcoal. The plant is mounted upon two railroad cars, the first of which carries the gas producer layout, while the second has the

remainder of the plant, including the cooler, scrubber, and other purifying devices.

The main apparatus on the front car consists of a pair of gas producers. Each of these has a heavy plate iron casing, which is lined with fire-brick. To remove slag and ash there are two doors in the front which are kept closed while the gas is being produced. On the top of the apparatus is a hopper for use in feeding in the coke. At the bottom of the producer are good-sized pipes which bring in the air-blast from the blowing chamber. The first of the two producers also has an oil spray for introducing the oil at the top part. The producer is filled up with coke, and hot air is sent in at the bottom, coming from a steam turbine driven blast-fan, this being worked by the steam from the locomotive. If need be, the blast-fan can also be driven by a gasoline motor or crude oil engine of the usual kind in the case of the portable plant, or with a stationary plant a gas engine, electric motor, or any suitable mechanical drive can be used.

Oil for the spray is supplied by a suitable oil pump, which feeds from a large tank on the car. It is necessary to heat this oil before feeding it into the producer, and the steam from the turbine is brought to the tank for this purpose, so that the heating is economically done. At the start of the apparatus both producers are filled with coke and fired up. By the use of the hot-air blast the coke is brought to a white heat, and during this time the coke gases are carried off through the opened top cover and escape into the air through the plate iron chimney. The blast is now stopped and the top cover closed down, whereupon the oil spray is set working, and the oil is transformed into oil-gas, this being obliged to pass through the heated coke of the two generators in succession. In this way all the light as well as heavy hydrocarbons are decomposed, and the result is a high grade of hydrogen gas containing from 90 to 96 per cent pure hydrogen. Before the producer is actually working to deliver the pure gas to the rest of the apparatus, care is taken to evacuate the gas which was already contained in the producers, and the first part of the newly produced hydrogen is allowed to escape by a special valve which is fitted on for this purpose, according to a patented method. During the usual working of the producers the passage of the gases through the hot mass of coke causes the temperature of the coke to become eventually lowered, and when it cools down below a certain point no more gas will be generated. When this is the case the oil feed is stopped, and the hot-air blast again turned on so as to fire up the coke mass as was done in the first place. Then the oil spray is turned on and the process repeated. Thus the method is an intermittent one, and consists in an alternate operation of the oil spray and hot blast. Firing up the coke by the blast usually takes two or three minutes during the run, that is, when the coke is still hot, then the gas production lasts for about twenty minutes, and so on.

From the second producer the gas goes by good sized piping into a device which is provided with a water seal in order to prevent a back flow of gas during the period when the hot-air blast goes through the producer. Care is taken in all cases to keep the hydrogen from becoming mixed with air. The gas then passes into the second car by means of coupled piping. On the front end of the car is mounted a well designed scrubber, which is designed with water flow so as to clear the gas of all mechanical impurities such as ash or soot. The scrubber consists of a plate iron case, which is filled up with the washing elements of patented make up, a water flow being introduced at the top, while the gas comes in at the bottom of the scrubber. Means are provided for effectively dividing up the gas flow in small streams so that it comes into as good contact as possible with the water.

Next the gas comes into a cleaner which works on a dry process, and is designed to remove any sulphur compounds contained in the gas. The gas is now sufficiently pure for many industrial purposes, as may be seen from the following analysis:—

	Per cent.
CO ₂	0.0
O	0.0
CO	2.7
CH ₄	0.0
H	96.0
N	1.3

The specific gravity of the gas is about 0.10. Next, the gas is freed from moisture by sending it through a sulphuric acid dryer, and lastly it passes through a heating furnace for removing the carbon monoxide, the furnace being heated by oil-gas. Then the gas goes to a cooler, which is built together with the first-mentioned scrubber. Analysis is then as follows:—

	Per cent.
CO ₂ , O, CH ₄	0.0
CO	0.4
H	98.4
N	1.2

Specific gravity = 0.087 to 0.092.

Firing up takes one to two hours, and the plant can run for months at a time, needing but two men. The plant follows the airship, and either supplies it direct or, where too far off, by a special outfit provided with steel gas bottles. To this end a third car can contain a compressor plant for charging the bottles. — Abridged from the *Scientific American*, cix., No. 24.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

THE REJUVENESCENCE OF THE POTATO.

The potato is a plant grown old and weakened by four hundred years of unsexed reproduction; it is the same plant that has been propagated for several centuries by the multiplication of its tubercles by slips or cuttings. How can the potato be rejuvenated? M. Sartory, Doctor of Science, of Nancy, and MM. Gralift and Thiebaut have examined this problem. In the name of these three scholars, M. Guignard, Professor of the Higher School of Pharmacy, has presented to the Academy of Sciences a paper, in which they show that edible tubercles can be obtained from the cultivated seed of the potato. However, this can only be arrived at by the help of certain fungi of the soil, which fix on to the plant and provoke the formation of the tubercles. In the spring of 1912, M. Sartory and his collaborators obtained from sowings, sixty plants which all bore tubercles in a greater or less number, the average size of which was about that of a walnut. Some of these potatoes weighed as much as 150 grms. Those that were in a good condition were able to be preserved and planted in 1913. They all produced vigorous plants free from disease. The new race is quite free from all imperfection, whereas the neighbouring potatoes were more or less attacked by various diseases. The putting into practice of this method of culture of potatoes by sowing will allow of the rapid regeneration of this precious tubercle; at the same time by crossings and selections it will be possible to obtain varieties presenting qualities desirable from an alimentary as well as from an industrial point of view. This discovery may have very important economical consequences.

THE BIRTH OF TUBERCLES.

To complete the paper presented by M. Guignard, Dr. Roux, Director of the Pasteur Institute, has informed the Academy of an interesting study by M. Magron, which shows that tuberisation takes place in the sown potato, thanks to a microscopic fungus belonging to the family of mucors, and which is moreover the parasite of the bitter-sweet. The tubercles are born only if these fungi penetrate into the prolongations of the subterranean roots

of the potato. The tuberisation is then thus caused by parasitism. The same facts are to be observed in orchids that can only be propagated by symbiosis. Fresh researches still kept secret will shortly revolutionise the culture of these precious and rare flowers.

BITTERNESS OF BURGUNDY WINES.

Certain of the finer quality wines of Burgundy have from time to time an inexplicable bitter taste, which is very disagreeable to connoisseurs and lovers of good wine. The origin of this bitterness had always remained unknown. A Professor of the Faculty of Science of Dijon has just made a most curious discovery concerning this fact. In a communication presented to the Academy by Prof. Armand Gautier, M. Voisinot shows that in drinkable waters there exists a microbe that possesses the property of dehydrating glycerin and giving acrolein, which becoming resinous produces the bitter that is so dangerous for the fine Burgundy wines. If this new ferment of M. Voisinot is, as he proves it to be, identical with that of the bitterness of these fine wines, it is easy to understand that it suffices to wash the bottles with spring water to introduce into those bottles the ferment that modifies so unfortunately, although only temporarily, the taste of these superior quality Burgundies.

A NEW INDICATOR OF FIRE-DAMP.

Fire-damp or coal-dust produce terrible catastrophes in mines. This carburetted hydrogen is inoffensive as long as it is only present in the mine in small quantities; but when the amount contained in the atmosphere exceeds the explosive limit, that is to say, 5.5 per cent, the miner's life is in danger if this explosive mixture should take fire. Safety lamps, those lamps of gauze wire invented by the English chemist Davy, have prevented many accidents. These lamps, which to-day are but little used on account of the weak light they give, may be employed as indicators of possible explosions. A practised eye, when the wick is lowered and when surrounded by a fire-damp atmosphere, can perceive a luminous halo, which becomes notably clearer and stronger as the explosive limit approaches. When large quantities of unbreathable gas arrive the lamp goes out. And yet many have tried to discover indicators or warners of carburetted hydrogen freed from all possibility of accidental inflammation. Two savants, Prof. Haber and Dr. Leiser, have just discovered an indicator which no longer addresses itself to the eye but to the ear, which organ acquires a great acuteness in the silence of the mine. They have imagined a whistle for fire-damp mines. It is a wire cylinder 25 cm. long and 5 cm. in diameter, formed by two whistles with closed lips, which are in unison, for one gas, and which are worked and put in movement by the same current. One of these whistles is filled with pure air. The tube of the other whistle is filled with the air of the mine. When the apparatus is made to act, if the air of the mine is pure only one sound is heard. If the gas of the whistle contains 1 per cent of methane, it is easy to hear two beats per second. When the quantity of methane increases, the beats augment rapidly, and in the neighbourhood of the explosive limit this phenomenon is transformed into a veritable trill. These differences of sound are easily perceived, and in the galleries of the mine they are still quite clear at a distance of 100 metres.

Catalytic Etherification in Aqueous Solution of Primary Alcohols of the Series $C_nH_{2n+2}O$. — F. Bodroux.—Formic, acetic, and propionic acids can be etherified by primary alcohols of the series $C_nH_{2n+2}O$ by distilling, in presence of a small quantity of catalyst, a mixture of the acid and alcohol diluted with a large quantity of water. The author has obtained a good yield of ethyl phenylacetate by mixing equal weights of phenylacetic acid, ethyl alcohol, and hydrochloric acid. — *Comptes Rendus*, clvii., No. 20.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 4th, 1913.

Prof. W. H. PERKIN, LL.D., F.R.S., President,
in the Chair.

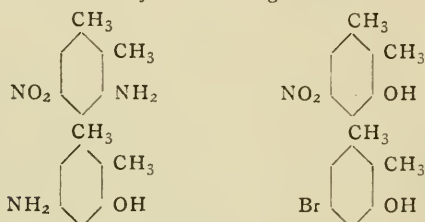
(Concluded from p. 35).

313. "The Optical Rotatory Power of Derivatives of Succinic Acid in Aqueous Solutions of Inorganic Salts." Part I. By GEORGE WILLIAM CLOUGH.

The specific rotations of *d*-tartaric acid, methyl *d*-tartrate, ethyl *d*-tartrate, and *d*-tartramide respectively have been measured at various temperatures in aqueous solutions of sodium and barium haloids. The values obtained are in all cases lower than those for the corresponding aqueous solutions. The results were discussed from the point of view of Armstrong and Walker's hypothesis (*Proc. Roy. Soc., A*, lxxxviii., 388).

314. "Derivatives of *o*-xylene. Part VI. 5-Bromo-*o*-3-xenol." By ARTHUR WILLIAM CROSSLEY.

5-Bromo-*o*-3-xenol has been synthesised by a series of reactions indicated by the following formulæ:—

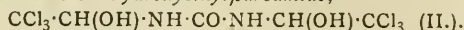


It crystallises from light petroleum (b. p. 40–60°) in radiating clusters of glistening needles, melting at 84°, and is identical with the bromoxylenol, of similar melting point, obtained by the action of phosphorus pentabromide on dimethyldihydroresorcin (*Trans.*, 1903, lxxxiii., 128).

The benzoyl derivative crystallises in rhombic plates, melting at 98°, and the *o*-nitrobenzoyl derivative separates from alcohol in transparent needles, melting at 128°.

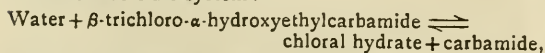
315. "The Condensation of Chloral Hydrate and Carbamide." By NOEL GUILBERT STEVENSON COPPIN and ARTHUR WALSH TITHERLEY.

The two derivatives obtained by Jacobson (*Annalen*, 1871, clvii., 246) in the condensation between chloral hydrate and carbamide are β -trichloro- α -hydroxyethyl-carbamide, $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ (I.), and di(β -trichloro- α -hydroxyethyl)carbamide,



They are formed by a reversible change whenever the reactants are present in equimolecular proportion in aqueous solution; with concentrated solutions the compound (I.) greatly predominates unless a mineral acid catalyst is present, which favours the production of (II.). When one molecular proportion of chloral hydrate acts on two of carbamide, however, the formation of the compound (II.) is prevented, unless a mineral acid is present. Both substances are slowly hydrolysed into chloral hydrate and carbamide on heating with water. Thus, in 50 per cent aqueous solution at 70, β -trichloro- α -hydroxyethyl-carbamide suffers decomposition to the extent of about 50 per cent in an hour. The mixture which separates on cooling contains about 70 per cent of compound (I.) and 30 per cent of compound (II.):—

In the reversible system:—



the true equilibrium is virtually never reached, owing to continual formation of di(β -trichloro- α -hydroxyethyl)-carbamide, which, being nearly insoluble, separates out.

β -Trichloroethylidenecarbamide, $\text{CCl}_3\cdot\text{CH}:\text{N}\cdot\text{CO}\cdot\text{NH}_2$ (m. p. 234°), is readily obtained from β -trichloro- α -hydroxyethylcarbamide by the action of acetic anhydride on its solution in alkali.

Trichloroethylidenecarbamide, previously obtained by Pinner and Lifschütz (*Ber.*, 1887, xx., 2346) from chloralcyanohydrin and carbamide, is produced slowly when β -trichloro- α -hydroxyethylcarbamide is heated at 100° with carbamide and acetic anhydride.

316. "The Action of Amino-acid Esters on Ethyl Dicarboxylglutaconate." By STANLEY ISAAC LEVY.

The reaction between ethyl dicarboxylglutaconate and organic derivatives of ammonia, which has been investigated by Ruhemann and his pupils, has now been extended to α -amino-acid esters. It has been found to apply generally to compounds of this class, and derivatives have been prepared from the esters of glycine, alanine, aminobutyric and aminoisobutyric acids, and leucine. With the exception of the first member of the series, ethyl glycylmethylenemalonate, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}:\text{C}(\text{CO}_2\text{Et})_2$, which is a colourless solid, these compounds are yellow, viscous oils; in chemical behaviour they closely resemble ethyl aminomethylenemalonate. Thus they are easily decomposed by acids or alkalis, and are not reduced by the zinc-copper couple; when heated with aniline, they yield the monoanilide of ethyl anilinomethylenemalonate.

317. "The Relationship between the Absorption Spectra and the Constitution of Ketones and their Derivatives" (Part I.). By GEORGE GERALD HENDERSON, JAMES ALEXANDER RUSSELL HENDERSON, and ISIDOR MORRIS HEILBRON.

The authors have re-examined the absorption spectra of a series of carefully purified aliphatic ketones, and have found that the characteristic absorption band of acetone is shown by all these compounds, and that the persistence of the band is in each case fully equal to that of the acetone band.

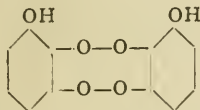
In order to account for these and other facts the authors suggest that the selective absorption of ketones is due to intramolecular vibrations caused by the momentary formation of unstable ring systems through the agency of free "partial valencies," which, under certain conditions, make their appearance on the atoms of the carbonyl group.

318. "Note on Purpurogallin." By ARTHUR GEORGE PERKIN.

In view of the fact that the author has been engaged for a long time with the study of purpurogallin (Perkin and Steven, *Trans.*, 1903, lxxxiii., 192; 1906, lxxxix., 802; A. G. and F. M. Perkin, *Ibid.*, 1904, lxxxv., 243; 1908, xcvi., 1186; A. G. Perkin, *Proc.*, 1905, xxi., 211; *Trans.*, 1912, ci., 803; 1913, ciii., 661), the recent paper of Nierenstein and Spiers (*Ber.*, 1913, xli., 3151) requires comment. These authors, who have repeated the earlier work of Perkin and Steven (*loc. cit.*), already partly confirmed by Herzig (*Monatsh.*, 1910, xxxi., 799), with identical result, claim to have established the presence of four hydroxyls in this compound, notwithstanding the fact that tetra-acetylurpurogallin, monoacetylurpurogallin trimethyl ether (*loc. cit.*, 1903), and purpurogallin tetramethyl ether (*loc. cit.*, 1905) have been prepared. Although acetylurpurogallin was described as yellow by Nietzki and Steinmann (*Ber.*, 1887, xx., 1277) and Perkin and Steven (*loc. cit.*), Herzig isolated this compound in the colourless condition, whereas Nierenstein and Spiers can only prepare an orange-yellow product. A colourless substance can, however, easily be obtained by crystallising from benzene with animal charcoal, although in the author's experience this purification is much more difficult to effect with acetic acid or alcohol. It is interesting to note that no distinction in melting-point can be observed between the yellow and colourless preparations, from which it appears possible that the pure acetyl compounds exist in two forms. This purpurogallin, regenerated from the latter variety, on reacylation with acetic anhydride

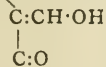
and pyridine yields the usual yellow product, which shows the same behaviour with solvents.

Nierenstein and Spiers refer also to the compound $C_6H_4O_3(?)$, first prepared by the oxidation of pyrogallol by means of isoamyl nitrite (*loc. cit.*, 1906), but more recently by means of *p*-benzoquinone (*loc. cit.*, 1913), which yields purpurogallin among other products when digested with boiling water. By the *p*-benzoquinone method (20 grms. of pyrogallol, 6 grms. of *p*-benzoquinone, and 15 cc. of absolute alcohol), the yield of 0.51 grm., although larger than that given by isoamyl nitrite (0.27 grm.), is so small that in the hope of the discovery of a better process which, however, has not been forthcoming, the author until recently hesitated to prepare a quantity of the material by these expensive methods. Although it suggested itself as possible that the production of this compound from pyrogallol was in reality due to the presence of traces of a second compound in this substance, this seems not to be the case, because pyrogallol, when submitted to the action of zinc dust and dilute acid, still reacts in the same way with *p*-benzoquinone. Whereas the constitution at first preferred for the compound $C_6H_4O_3(?)$ was that of a hydroxy-*o*-benzoquinone, Willstätter and Müller (*Ber.*, 1911, xlv., 2180) consider this to be unlikely, and further work now in progress favours the second or peroxide formula, already alluded to in the earlier communication.



Nierenstein and Spiers have again examined the product of the distillation of purpurogallin with zinc dust, although Nietzki and Steinmann and also Perkin and Steven obtained naphthalene thereby, and it has been very recently shown that by the reduction of purpurogallone both β -naphthol and 2:3-dihydroxynaphthalene can be produced. If purpurogallin, as now seems probable, is in reality a naphthalene derivative, the simple expression $C_{10}H_4(OH)_4CO$ is only available for it. In such a case it has suggested itself to the author among other con-

siderations that the *o*-quinonoid grouping,



is present, because the isomeric purpurogallone derived from it by the action of alkali at a high temperature, which has the properties of a trihydroxynaphthalene-carboxylic acid, can thus be regarded as a product of simultaneous oxidation and reduction. Such a grouping would also account for the comparative resistance of the fourth hydroxyl in purpurogallin to methylation, and again, the formation of the colourless acetyl and tetramethyl derivatives could be explained on the assumption that these exist in the tautomeric hydroxy aldehydic

condition. A formula involving the grouping



also suggests itself, and these points are mentioned here in that the work on which the author is now engaged, and which consists mainly of a study of the oxidation of the purpurogallin methyl ethers, involving as it does the preparation of large quantities of material, will occupy a considerable time.

319. "1-Epicamphor (1- β -camphor). By JULIUS BREDT and WILLIAM HENRY PERKIN, jun.

A detailed description of work of which a preliminary account has already appeared (*Proc.*, 1912, xxviii., 56).

320. "The Action of Hydrogen Peroxide on the Sodium Alkyl Thiosulphates." By DOUGLAS FRANK TWISS.

Dibenzyl diselenide has been submitted to oxidation (both electrolytic and by hydrogen peroxide) in the hope of producing compounds of the selenoxide, selenone, or selenonium salt class (compare Fichter and Sjöstedt, *Ber.*, 1910, xliii., 3422), but the result of such treatment was to eliminate the selenium from the molecule either in the free state or as selenious acid.

In consequence of the lack of success attendant on experiments in this direction, the effect of oxidation of sodium or potassium alkyl selenosulphates was considered as a possible process for the achievement of the desired end. The action of hydrogen peroxide was therefore first tried with sodium alkyl thiosulphates, when it was found that in acid solution this process gives rise to excellent yields of the corresponding disulphides even at the ordinary temperature. Dibenzyl, di-*o*-nitrobenzyl, di-*p*-nitrobenzyl, and diallyl disulphides were prepared in this manner. Under similar treatment, potassium *o*-nitrobenzyl selenosulphate produced di-*o*-nitrobenzyl diselenide.

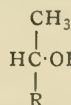
321. "Synthesis of *d*- and *l*-Sylvestrene." By WALTER NORMAN HOWARTH and WILLIAM HENRY PERKIN, jun.

A detailed description of work of which a preliminary account has appeared (*Proc.*, 1910, xxvi., 97; 1913, xxix., 223).

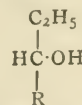
322. "Note on the Configurations of the Optically Active Normal Secondary Alcohols." By GEORGE WILLIAM CLOUGH.

Pickard and Kenyon have prepared ten optically active carbinols of the series $CH_3 \cdot CH(OH) \cdot R$ (the "methyl" series), eight of the series $CH(CH_3)_2 \cdot CH(OH) \cdot R$ (the "isopropyl" series), and thirteen of the series $C_2H_5 \cdot CH(OH) \cdot R$ (the "ethyl" series). The simplest carbinol of the "methyl" series and of the "ethyl" series is methylethylcarbinol. Pickard and Kenyon have made a comparison of the molecular rotatory powers of the dextro-rotatory carbinols of the "methyl" and of the "ethyl" series, and have selected the dextro-rotatory form of methylethylcarbinol for comparison with the dextro-rotatory carbinols of both series (*Trans.*, 1911, xcix., 45; 1912, ci., 620; 1913, ciii., 1923).

Although it is impossible to state with certainty that the carbinols possessing the same sign of rotation are configuratively similar, it appears highly probable that in the case of the higher members of a series similarity of sign does indicate similarity of configuration. The assumption may therefore be made (and the course of the curves for the molecular rotations strongly supports this view) that in the "methyl" series where $R > CH_3$ (that is, in all cases), and in the "ethyl" series where $R > C_2H_5$, similarity of sign of rotation accompanies similarity of configuration. Moreover, if the two series of carbinols, $CH_3 \cdot CH(OH) \cdot R$ and $C_2H_5 \cdot CH(OH) \cdot R$, are compared, it appears exceedingly probable from a consideration of the curves representing the molecular rotations in the homogeneous state, in benzene solution and in ethyl-alcoholic solution respectively, that the higher dextro-rotatory carbinols of the "methyl" series are configuratively similar to the dextro-rotatory carbinols of the "ethyl" series. Thus, if $R > C_2H_5$, the corresponding dextro-rotatory carbinols of the two series may be configuratively represented by the formulæ—

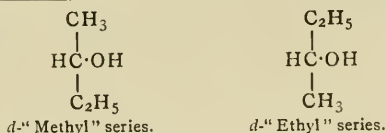


d-"Methyl" series.



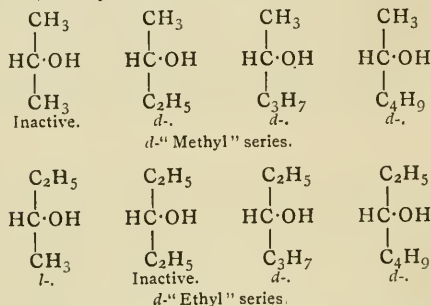
d-"Ethyl" series.

The simplest optically active members of the *d*-"methyl" and *d*-"ethyl" series may therefore be represented by the formulæ—



In other words, the simplest member of the d-"methyl" series is the optical antipode of the simplest member of the d-"ethyl" series. The assumption which has already been made that similarity of sign in the "methyl" series always indicates similarity of configuration leads to the view that d-methylethylcarbinol is the simplest optically active member of the d-"methyl" series. Consequently, l-methylethylcarbinol is the first optically active member of the d-"ethyl" series. We therefore arrive at the apparent paradox that the simplest members of the two configurationally similar series are enantiomorphous forms of the same substance.

The earlier members of the d-"methyl" and d-"ethyl" series may be represented thus:—



In the "ethyl" series, for the first member $R < \text{C}_2\text{H}_5$, for the second $R = \text{C}_2\text{H}_5$, whilst for the other members $R > \text{C}_2\text{H}_5$. It is therefore not surprising that there should be a change of sign in the passage from the first to the third member of this series.

The view here advanced is confirmed by reference to the curves of Pickard and Kenyon (*Trans.*, 1913, ciii., 1924, 1926, 1929). The curves in Figs. 1 and 2 for the molecular rotations of the d-"ethyl" series show a marked abnormality in the case of the first member. If the value for l-methylethylcarbinol is substituted for that of the d-carbinol, the curves exhibit much greater regularity. The curve (Fig. 4) for the d-"methyl" series shows no abnormality in the first member, for d-methylethylcarbinol has the same configuration as the other d-carbinols of this series.

Attention may also be drawn to the values for the molecular rotation of the hydrogen phthalic esters of the dextro-rotatory carbinols, $\text{C}_2\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{R}$, in ethyl-alcoholic solution. The value for the rotation of the ester with $R = \text{CH}_3$ is $[\text{M}]_D + 86.5^\circ$, with $R = \text{C}_3\text{H}_7$, $[\text{M}]_D + 9.42^\circ$, whilst with $R = \text{C}_4\text{H}_9$, $[\text{M}]_D + 52.3^\circ$. It is evident that the value for the ester of l-methylethylcarbinol should be compared with those for the esters of the dextro-rotatory carbinols of the "ethyl" series (compare Fig. 1, *loc. cit.*).

The temperature coefficients for the rotations of the two series of d-carbinols are also of interest in this connexion. The specific rotations of the dextro-rotatory alcohols of the methyl series (including d-methylethylcarbinol) diminish with rise of temperature (*Trans.*, 1911, xcix., 50), whereas the values for the dextro-rotatory carbinols (up to ethyl-nonylcarbinol) increase with rise of temperature, with the exception of d-methylethylcarbinol. If the view is accepted that l-methylethylcarbinol is the first member of the d-"ethyl" series the temperature-rotation curves for the earlier members of this series are similar in character.

These considerations show the impossibility of expressing the relative configurations of a series of optically active compounds by the designations d and l.

323. "The Surface Tension of Mixtures. Part I. Mixtures of partly Miscible Liquids and the Influence of Solubility." By RALPH PALLISER WORLEY.

Experiments were made with the object of throwing light on peculiarities noticed in the surface tensions of weak solutions of some liquids which are only partly miscible with water.

The surface tension was measured by means of the capillary rise method, the liquids examined being aniline, phenol, and isobutyl alcohol. The decrease of the solubility of aniline in water produced by the addition of common salt had the effect of greatly lowering the surface tension, the final value being not far above that of pure aniline. In the case of aniline and phenol the surface tensions of some of the more concentrated solutions rose with increasing temperature, whilst the surface tensions of none of the solutions, not even the weakest, fell normally, that is, similarly to that of a pure liquid. On the other hand, the surface tension of all solutions of isobutyl alcohol fell regularly.

This difference of behaviour has been accounted for by the different behaviour exhibited towards water with increase of temperature. Whereas the solubility of aniline and phenol increases with rise of temperature, the solubility of isobutyl alcohol decreases up to 75° , and then increases rapidly until the critical solution temperature is reached. These results point to the fact, therefore, that the low surface tension of solutions of partly miscible liquids is due to the lack of solubility of the solute. The reason of this is that liquids when near their limit of solubility form solutions which are rather of the nature of colloidal than of true solutions.

324. "The Surface Tension of Mixtures. Part II. Mixtures of perfectly Miscible Liquids and the Relation between their Surface Tensions and Vapour Pressures." By RALPH PALLISER WORLEY.

A relation exists between the surface tension and the vapour pressure of a liquid. The object of the present research was to find out whether in mixtures of liquids deviations from a general law governing vapour pressures were accompanied by corresponding deviations in the case of surface tensions.

The following mixtures were examined:—(1) *Benzene and Ethylene Dichloride*.—The surface tensions were found to agree with those calculated from the admixture rule. So also do the vapour pressures agree with those calculated (Zawidski). (2) *Carbon Disulphide and Acetone*.—The surface tensions were found to be below the calculated values, and the curve to tend towards a minimum. The vapour pressures are much greater than those calculated, and the curve passes through a maximum. (3) *Acetic Acid and Pyridine*.—The surface tensions were much greater than those calculated, and the curve tended towards a maximum value. The vapour pressures are much below those calculated, and the curve forms a minimum.

It seems therefore that when a mixture obeys one admixture rule it obeys the other also; when the surface tensions are greater than those calculated the vapour pressures are less, and vice versa.

Additional proof was given by mixtures of benzene and carbon tetrachloride, and the homologous series of alcohols and water.

From experiments with sulphur and carbon disulphide, it appears that the relations hold good for all mixtures.

325. "The Tautomerism of Thioanilides." By PERCY MAY.

Although the thioanilides are usually represented as thioketones, $\text{R}\cdot\text{NH}\cdot\text{CS}\cdot\text{R}'$, yet in many respects they react as iminomercaptans, $\text{R}\cdot\text{N}:\text{C}(\text{SH})\cdot\text{R}'$. The methyl derivatives corresponding with both forms were prepared in the case of thiobenzanilide and thioacetanilide, and their absorption spectra were compared with those of the parent substances in the light of Thiele's theory of "conjugated" unsaturated linkings. When thiobenzanilide was sub-

jected to the action of methylating agents in neutral solvents, the sulphur was eliminated as methyl sulphide.

N-Methylthiobenzanilide was obtained by the action of phosphorus sulphide on methylbenzanilide, and crystallises from alcohol in small yellow cubes, melting at $90-91^{\circ}$.

S-Methylthiobenzanilide was obtained by the action of methyl sulphate on thiobenzanilide in alkaline solution, and crystallises from aqueous alcohol in colourless needles, melting at $63-64^{\circ}$.

326. "The Determination of Viscosity." By MALCOLM PERCIVAL APPLEBEY.

In reply to the criticism of Bingham (*Trans.*, 1913, ciii., 959), the author discussed the phenomena of flow in the Ostwald viscometer and the experimental conditions requisite for obtaining accurate determinations.

327. "Lead Cyanide." By NALINI MOHAN GUPTA.

According to Rammelsberg (D.R.P. 139456) the compound $Pb(CN)_2$ is formed by precipitating a solution of a lead salt with aqueous hydrocyanic acid or a soluble cyanide, whereas Kugler (*Annalen*, 1848, lxvi., 63) states that a basic salt, $Pb(CN)_2 \cdot 2PbO \cdot H_2O$, is formed by precipitation from an ammoniacal solution. It appears, however, to be generally recognised that the precipitate formed by the interaction of cyanides and lead salts in aqueous solution varies in composition with the concentration of the solutions employed, a fact which the author has confirmed.

Lead cyanide was decomposed by hydrogen sulphide, and the hydrogen cyanide was led into water through a U tube containing lead cyanide. To remove any traces of hydrogen sulphide from the aqueous hydrocyanic acid, some lead cyanide was added to it, and the solution shaken. As no trace of hydrogen sulphide was present no lead sulphide was formed; but after filtering this solution it was found that it contained a considerable quantity of lead. It was evident that lead cyanide, which is not appreciably soluble in cold water, is soluble in aqueous hydrocyanic acid, and it was expected that this solution would, on evaporation, deposit pure lead cyanide free from oxide.

About 250 cc. of a 5 per cent solution of hydrocyanic acid were heated to boiling with a small quantity of precipitated lead cyanide under reflux. After about half-an-hour the solution was filtered and allowed to evaporate slowly in a desiccator. The deep yellow needle-shaped crystals which separated were collected and dried in a vacuum.

Lead cyanide, even when powdered, appears to be unattacked by concentrated nitric and sulphuric acids in the cold. On adding water to a crystal, the insoluble oxycyanide is formed, and the water becomes cloudy.

A weighed quantity of the substance was heated for some hours to 120° ; there was no loss in weight.

For the estimation of cyanogen and lead a weighed quantity of the substance was heated in a water-bath in a sealed tube with a weighed excess of silver nitrate and a little nitric acid. The silver cyanide was collected and weighed. The silver remaining in solution was precipitated and weighed as silver chloride, which served as a check on the weight of the silver cyanide. Finally the filtrate was evaporated with sulphuric acid, and the lead sulphate weighed. Two different samples were analysed:—

I. 0.1838 gave 0.1883 AgCN and 0.2137 $PbSO_4$.
CN = 19.90; Pb = 79.42.

II. 0.2272 gave 0.2340 AgCN and 0.2638 $PbSO_4$.
CN = 20.00; Pb = 79.32.

$Pb(CN)_2$ requires CN = 20.07; Pb = 79.92 per cent.

The crystals consisted therefore of lead cyanide having the formula $Pb(CN)_2$.

328. "Contributions to the Theory of Solutions. The Intermiscibility of Liquids." By JOHN HOLMES.

The relative solubilities of liquids have been correlated with their molecular volumes as ascertained by a method

(previously described) based on the deviations observed in the additive relations of mixtures of liquids.

On the assumption that a pure liquid consists of a collection of like spherical molecules, it is deduced that any liquids, the molecular spheres of which have equal radii, should be miscible in all proportions. In binary mixtures this mutual miscibility continues until the ratio of the respective radii reaches 1.618, when the border line of partial miscibility is reached. When the ratio is greater than this value, the mixture separates into layers, in each of which the distribution of molecules is dependent on the further change in this ratio until it reaches 2.414, beyond which the liquids should be immiscible.

The curves of volume change calculated from densities available for various mixtures of liquids have been drawn, and the molecular volumes deduced from the ascertained complexities are compared with those required theoretically, on the above hypothesis, for their relative solubilities. The molecular complexities found for these liquids differ from those generally accepted, but the corresponding molecular volumes approximate closely to solubility requirements, and render it probable that the intermiscibility of liquids is a function of molecular volume and independent of chemical constitution.

The experimental data include densities at 15° of mixtures of isobutyric acid with water, ethyl tartrate with water, and ethyl tartrate with glycerol; also densities at 25° of mixtures of chloroform with *n*-amyl alcohol and acetone. The critical temperatures of solution were determined for nicotine and water, and for carbon disulphide and ethyl tartrate when mixed in the proportion of 1 to 2 molecules (liquid) respectively. Volume changes in aqueous ethyl alcohol mixtures are compared with the corresponding differences from the theoretical values for refractive indices.

329. "A Contribution to the Study of the Constitution of the Methyl Pentoses. Part I. The Synthesis of an *i*-Methyl Tetrose and an *i*-Methyl Tetritol." By ROBERT GILMOUR.

An account was given of the isolation of an inactive methyl tetrose by reducing dihydroxyvalerolactone with sodium amalgam in acid solution. The free sugar has been prepared, and found to be a strongly reducing pale yellow syrup.

Methyl tetrosazone forms pale yellow needles, melting at $140-142^{\circ}$. Methyl tetrosephenylbenzylhydrazone forms colourless needles, melting at $99-100^{\circ}$. It was shown that the reduction of dihydroxyvalerolactone yields as the main product a methyl tetritol, along with only a small amount of the tetrose. The tetrabenzoyle derivative of methyl tetritol melts at $136-137^{\circ}$. In addition the methyl tetritol has been oxidised by Fenton's method to the methyl tetrose, which was isolated in the form of the phenyl benzylhydrazone.

A racemic *brucine* salt of the methyltetrone acid was also described (m. p. $180-181^{\circ}$) as well as a dimethoxyvalerolactone (m. p. $59-60^{\circ}$), which was obtained by methylating dihydroxyvalerolactone.

Further, an account was given of a method which it is proposed to adopt for the preparation of other methyl tetroses, and their importance as a means of determining the constitution of naturally occurring methyl pentoses was indicated.

Solubility in the Solid State of Nitrates, Sulphates, and Carbonates at High Temperatures.—M. Amadori.—The solubility of sulphates, carbonates, and nitrates in the solid state is either very small or negligible in the cases of the lithium, sodium, and potassium salts. The nitrates crystallise with the carbonates, and with the sulphates in eutectics constituted almost exclusively of nitrate at a temperature only $3-10^{\circ}$ lower than that of the solidification of the nitrate. No compounds are formed either at the temperature of solidification nor at a lower temperature between sulphate and nitrate, nor between carbonate and nitrate.—*Atti Reale Accad. Lincei*, 1913, xxii., No 7.

NOTICES OF BOOKS.

A Dictionary of Applied Chemistry. By Sir EDWARD THORPE, C.B., LL.D., F.R.S. Assisted by Eminent Contributors. Revised and Enlarged Edition. Vol. V. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913

This volume, covering Sodium—Z, brings to an end the last edition of Thorpe's Dictionary of Applied Chemistry. It fully maintains the high standard of excellence which the previous volumes have reached, and contains a number of lengthy articles by authors of world-wide fame. These include, to mention only a few, articles on Spectrum Analysis, by Prof. E. C. C. Baly; on Soils, by Dr. A. D. Hall; Synthetic Drugs, by Dr. Virgil Coblenz; Vegeto-alkaloids by Prof. W. R. Dunstan; Vat Dyes, by Dr. E. Knecht; Water, by Dr. P. F. Frankland; and Terpenes, by Sir W. A. Tilden.

The Progress of Scientific Chemistry in Our Own Times. By Sir WILLIAM A. TILDEN, F.R.S., D.Sc.(Lond.), Sc.D.(Dub.), D.Sc.(Vict.), LL.D.(Birm.). Second Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

THE author of this book was confronted with a very difficult task when he was called upon to deliver a short course of lectures to working men, and chose as his subject the progress of chemistry from 1837 to 1897. However, he proved to be more than equal to the occasion, and this book, based upon the lectures, is a triumphant witness to his skill in making a highly technical and somewhat obscure subject clear to readers who cannot be supposed to possess more than a slight acquaintance with the elements of chemistry. In the second edition, while the matter has been brought up to date, the general plan has not been in any way altered, and the book will give the student and the general reader a clear idea of the growth of modern chemical theory.

A Treatise on Chemistry. By Sir HENRY ROSCOE, F.R.S., and C. SCHORLEMMER, F.R.S. Volume II. *The Metals.* New Editions. Completely Revised by the Right Hon. Sir HENRY ROSCOE and others. London: Macmillan and Co., Ltd. 1913.

THE general plan and arrangement of the original edition of this well-known standard treatise have been preserved in the fifth edition, but the whole has undergone a careful revision. Mr. T. V. Barker has made alterations and additions in the chapter on crystallography, and Dr. Makower deals with recent important researches in radio-activity, while other specialists have rendered assistance to the author in revising and amplifying the text in accordance with modern knowledge.

A Text-book of Physics. By J. H. POYNTING, Sc.D., F.R.S., and Sir J. J. THOMSON, O.M., M.A., F.R.S. Volume I. "Properties of Matter." Sixth Edition. London: Charles Griffin and Co., Ltd. 1913.

THE fifth edition of this treatise on physics was issued only a very short time ago, and hence in the sixth edition it has not been found necessary to make any alterations beyond the addition of several important notes. In many respects it is a model text-book for students who, while possessing an elementary knowledge of physics, have not yet reached the stage when they can profitably attack advanced treatises. The text is remarkably clear and the authors' explanations are both lucid and graphic.

Carbon Dioxide Snow. By J. HALL-EDWARDS, L.R.C.P., F.R.S. (Edin.), Hon. F.R.P.S. London: Simpkin, Marshall, Hamilton, Kent, and Co., Ltd. 1913.

THE author of this little book has done much to render the application of carbon dioxide snow more practicable and economical, and he has had much experience in using it

therapeutically. He describes at some length the apparatus employed, and points out the many advantages which the snow possesses over liquid air in dermatology. He also discusses the results produced in the case of different diseases of the skin, &c., and gives a very impartial account of the effects of treatment with the snow. Details of methods of application are included, with illustrations, and allusion is made to all the necessary precautions in handling the material and in after treatment.

The Silicates in Chemistry and Commerce. By Dr. W. ASCH and Dr. D. ASCH. Translated by ALFRED B. SEARLE. London: Constable and Co., Ltd. 1913.

THIS book is based on a thesis submitted to the University of Göttingen, and there awarded a prize in 1903 in connection with the Benek Bequest. The thesis has been much enlarged by the insertion of additional confirmatory material, and the translator has also added many explanatory or critical notes. The authors began their thesis with a comprehensive survey of the existing theories concerning the aluminosilicates, and succeeded in showing that all such theories were incompatible with the facts, except one, viz., that the aluminosilicates are complex acids or salts. Although objections can be brought forward to this view, it seemed not improbable that they are only apparent, and the authors claim that their hypothesis regarding the union of the atoms in the anhydrides of the aluminosilicates satisfactorily meets all criticisms. The theory of hexite and pentite rings (rings containing six or five aluminium or silicon and oxygen atoms) is explained, and its application not only to aluminosilicates but also to other complex acids, e.g., molybdic and tungstic acids, is worked out in detail. The constitutions of clays, ultramarines, Portland cements, glasses, &c., are explained on the basis of the theory. The bearing of the hexite-pentite theory on the question of the constitution of the atom and its extension to a stereo chemical theory are also discussed, and the authors' hypothesis is undoubtedly very ingenious and requires careful consideration.

Cement, Concrete, and Bricks. By ALFRED B. SEARLE. London: Constable and Co., Ltd. 1913.

THIS book contains an excellent account of the chemistry of the manufacture of cements, concretes, and bricks. The genetic relations between these three classes of building materials are clearly pointed out, and modern theories regarding the chemical and physical changes which occur in the setting and hardening of cements and the drying and burning of bricks are discussed. The author's knowledge of the scientific aspects of the brick industry and the questions involved in it is unique, and he places his experience and his wide knowledge freely at the disposal of his readers. The book is not intended for the unscientific man, and a good grounding in chemistry is required in order that it may be used profitably; it contains many suggestions as to the directions in which fruitful research may be undertaken. Methods of performing tests on concretes and cements and the making of special kinds of bricks are described in detail.

The Employment of Sodium Bisulphite in the Preparation of Plantation Rubber. By C. BEADLE, H. P. STEVENS, and S. MORGAN.

THIS pamphlet contains an article which has been reprinted from the *Indianrubber Journal* for August 2nd, 1913. The authors describe shortly the tests they have performed with many specimens of rubbers prepared with and without sodium bisulphite; these tests show that on the whole the former are of slightly better quality. Hence the authors consider that the bisulphite should be regarded as a cheap and effective agent for preserving the pale colour of rubber. They have observed that rubbers prepared with sodium bisulphite tend to dry more slowly than other specimens.

The Journal of the Alchemical Society. Vol. II., Part VII.
London: H. K. Lewis.

The November number of the *Journal of the Alchemical Society* contains an interesting paper which was read by M^{me}. de Steiger at the General Meeting. The subject of the paper was "The Hermetic Mystery," and M^{me}. de Steiger proved herself to be an able exponent of her theory concerning the true aims of the Royal Art of Alchemy. A short abstract is also given of the discussion which followed the paper.

The British Empire Universities Modern English Illustrated Dictionary. Revised under the Chief Editorship of EDWARD D. PRICE. London, Toronto, New York: The Syndicate Publishing Co., 1914.

This dictionary is very much more than a mere catalogue of words and their meanings, and it may safely be used to give reliable and up-to-date information upon a great variety of subjects. The words given in the dictionary proper have been carefully chosen for utility and general information; plain rules for pronunciation are given, and the definitions are always precise and perfectly clear. In addition, there is a lengthy article on the principles of English Grammar, and Sir Arthur Quiller-Couch contributes a short history of English literature. Complete glossaries of the terms used in certain sports have been compiled for the dictionary by well-known specialists, and there are also lists of synonyms, antonyms, foreign words and phrases, contractions and abbreviations, famous characters in prose and poetry, &c. The book is printed in excellently clear type and is well bound. The illustrations appear to be its least satisfactory feature. Thus, for example, from the plate showing different breeds of dogs the pug would seem to be about the same size as the collie, and the "up-to-date barn" houses a number of cows, although a barn is correctly defined.

The Freezing-point Lowering, Conductivity, and Viscosity of Solutions of certain Electrolytes in Water, Methyl Alcohol, Ethyl Alcohol, Acetone, and Glycerol, and in Mixtures of these Solvents with one Another. By HARRY C. JONES and Collaborators. Washington, D.C.: The Carnegie Institution. 1913.

In this monograph the continuation of the experiments which have been in progress in the Chemical Laboratory of the Johns Hopkins University during the last twelve years is described in detail, and the book may be regarded as a supplement to No. 80 of the Publications of the Carnegie Institution of Washington. Full accounts are given of the experimental work which has been done by the various collaborators, each of whom has devoted himself for periods ranging from one and a-half to two and a-half years to the elucidation of one or two questions. The results obtained in the different series of researches are also discussed in relation to one another, and some important general conclusions are drawn, especially as regards the conductivity of the dissolved electrolyte and the viscosity of the pure and mixed solvents. The work included a particularly interesting series of systematic investigations of the properties of solutions in glycerol.

Tabelle der wichtigsten Organischen Verbindungen geordnet nach Schmelzpunkten. ("Index of the Most Important Organic Compounds Arranged in Order of their Melting-points"). By Dr. RICHARD KEMPE. Braunschweig: Friedrich Vieweg und Sohn. 1913. (Mk. 8.80).

THERE are some novel features about this index which will commend themselves to those who are in the position of frequently wanting to identify organic compounds as rapidly and easily as possible. The book contains a list of some 2500 organic compounds of scientific or technical importance arranged in order of increasing melting-point, the temperatures ranging from -184° to $+419^{\circ}$, and it is claimed that in nearly all cases a determination of the melting-point will enable the chemist to ascertain the

formula of the substance under investigation. For each substance the boiling-point, colour, and abbreviated constitutional formula are tabulated; also a reference to the original article in which the substance was described and to Beilstein's Tables. In cases in which different melting-points have been stated for the same compound an attempt has been made to estimate the relative value of the data and to give the temperature which is most probably correct, while if it is impossible to decide between two or more they are both given, with cross references. From this short description the great usefulness of the book will at once be recognised, particularly in cases in which only small quantities of a substance are available for identification and an elementary analysis is impossible.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clvii., No. 21, November 24, 1913.

Alkylation of Thujone and Isothujone using Sodamide.—A. Haller.—The alkylation of thujone in presence of sodamide stops at the disubstituted product, this ketone, like menthone, being incapable of trimethylation. Like menthone the ketone will give a triallyl derivative. Although isothujone does give dimethyl and monoallylisothujone, it yields chiefly condensation products. From these experiments it appears that thujone contains the group $\begin{array}{c} | \\ -CH-CO-CH_2 \end{array}$ and isothujone the group $\begin{array}{c} || \\ -C-COCH_2 \end{array}$.

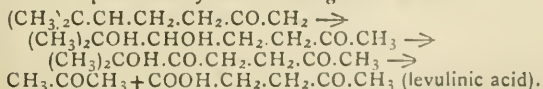
Hydrates of Silver Fluoride.—A. Guntz and A. A. Guntz, jun.—When a neutral solution containing 120 grms. of AgF in 100 grms. of water is slowly evaporated at 10° AgF $\cdot$ 4H $_2$ O separates out. Below 18.5° this is the only fluoride stable in neutral solution. When it is strongly supersaturated it may deposit crystals of AgF $\cdot$ 2H $_2$ O. If a solution containing 170 grms. AgF to 100 grms. of water is allowed to evaporate between 18° and 38° the hydrate AgF $\cdot$ 2H $_2$ O separates in deliquescent crystals. After adding crystals of AgF $\cdot$ H $_2$ O to a saturated neutral solution of AgF and evaporating between 26° and 36° octahedra of AgF $\cdot$ H $_2$ O are obtained. In the same conditions at the ordinary temperature crystals of 3AgF $\cdot$ 5H $_2$ O may separate. These two last hydrates are unstable and readily give the anhydrous fluoride, which is also obtained by drying any of the preceding hydrates *in vacuo* over sulphuric acid.

No. 22, December 1, 1913.

This number contains no chemical matter.

Atti della Reale Accademia dei Lincei.
Vol. xxii. [ii.], No. 8, 1913.

Chemical Action of Light.—G. Ciamician and P. Silber.—When acetone, cyclohexanone, and its three methyl derivatives and methylheptenone are exposed to light in the presence of oxygen, the latter attacks the molecule in the same way as in the hydrolysis which accompanies the process of autooxidation, except in the cases of methylheptenone, which is not hydrolysed in light, and of acetone. With heptenone the autooxidation can be represented by the following scheme:—



Formation of Compounds of Fluorides, Chlorides, and Carbonates of Metals.—M. Amadori.—Of the couples NaF—Na $_2$ CO $_3$, KF—K $_2$ CO $_3$, NaCl—Na $_2$ CO $_3$, KCl—K $_2$ CO $_3$, only the second gives a compound in equi-

molecular proportions on the solidification of the mixed melt. Fluorides and sulphates of both potassium and sodium form stable compounds in equimolecular proportions, and thus the formation of compounds is influenced both by the nature of the acid and that of the base. Chlorides and carbonates give no compounds but simply eutectics.

MISCELLANEOUS.

Method of Disintegrating Metals and their Oxides into a Colloidal State.—Masamichi Kimura.—When a piece of metal heated in a Bunsen burner or by an electric current is suddenly introduced into water a number of fine particles is produced. A few drops of distilled water were first examined with the ultramicroscope and found to contain no colloidal particles. A piece of platinum wire was heated to a white heat by an electric current and put into the water; this process was repeated, and a drop of the water was then examined under the microscope, when many fine particles showing the Brownian movement were observed. From the investigation of the cataphoresis it was found that some particles travelled towards the cathode while others proceeded in the opposite direction. Similar experiments with silver and copper gave the same results.—*Memoirs of the College of Science and Engineering, Kyoto Imperial University*, 1913, v., No. 6.

Lawes and Gilbert Centenary Fund.—During the Christmas holidays the Lawes and Gilbert Centenary Fund Committee ceased work so as not to interfere with the ordinary Christmas appeals; it has now begun work again to collect the last £1600 needed to complete the scheme. The object of the Centenary Fund is to build and equip a satisfactory laboratory for the prosecution of researches in agricultural chemistry, a subject largely founded on the experiments of Lawes, who was born just 100 years ago, and of Gilbert, who was born three years later. These investigators founded the Rothamsted Experimental Station, the oldest and for many years the best equipped agricultural experiment station in the world. Rothamsted has maintained its high position in respect of its staff and its field plots, but it has fallen behind in laboratory accommodation, and a serious effort is now being made to remedy this defect. The Committee has ascertained that a satisfactory laboratory can be erected and equipped for £12,000, and it has decided to collect the money, and to put up the laboratory this year in commemoration of the centenary of the birth of the founders. Its efforts have been so far successful that only £1600 is now required, and an urgent appeal is addressed to all interested in agricultural science to aid the Committee in closing the list so that the work can be put in hand at an early date. Subscriptions should be sent to the Secretary, Rothamsted Experimental Station, Harpenden, Herts.

Royal Society of Arts.—The Swiney Prize.—The Swiney Prize for Jurisprudence has been awarded to Mr. John W. Salmond, K.C., Solicitor General for "New Zealand, for his work "Jurisprudence." The prize consists of a sum of £100 contained in a silver cup of the same value. It was founded in 1844 under the will of Dr. George Swiney, a somewhat eccentric medical man, who left £5000 Three per cent Consols to the Society in order that the prize might be awarded on every fifth anniversary of his death to the author of the best published work on Jurisprudence. Although the bequest was made to the Society of Arts alone, Dr. Swiney appointed as adjudicators the members of the Society and the Fellows of the Royal College of Physicians. An arrangement was made by the adjudicators that the award should be given alternately for Medical and General Jurisprudence. The cup is made after a design prepared in 1849, for the first

award, by Daniel Maclise, R.A., and the execution has been entrusted to Messrs. Garrard. The prize has been awarded on thirteen previous occasions, among the recipients being Sir Henry Sumner Maine, K.C.B., D.C.L., for his "Ancient Law"; The Rt. Hon. Sir Robert Joseph Phillimore, D.C.L., for his "Commentaries on International Law"; Thomas Erskine Holland, D.C.L., for his "Elements of Jurisprudence"; and Sir Frederick Pollock, Bart., and Professor F. W. Maitland, for their "History of English Law before Edward the First." It may be mentioned that in addition to this bequest to the Royal Society of Arts, Dr. Swiney also left a similar sum of £5000 to the Trustees of the British Museum for the establishment of a lectureship in geology.

New Catalogue.—Messrs. Crosby Lockwood and Son (7, Stationers' Hall Court, Ludgate Hill, and 5, Broadway, Westminster), have recently issued a new catalogue of the Scientific, Technical, and Industrial books published by them. The catalogue, which is well illustrated, contains extracts from some book reviews, and Messrs. Crosby Lockwood and Son will be pleased to send it post free to any readers of the CHEMICAL NEWS who may desire it.

Literary Intelligence.—Messrs. J. and A. Churchill have just ready for publication Volume VIII. of the new edition of "Allen's Commercial Organic Analysis." This volume has been re-written under the editorship of Mr. W. A. Davis, B.Sc., and Mr. S. S. Sadtler, S.B. The subjects and authors are as follows:—"Enzymes, Proteins of Plants," by E. Frankland Armstrong; "The Proteins and Albuminoid Substances, Digestion Products of the Proteins," by S. B. Schryver; "Proteins of Milk," by L. L. Van Slyke; "Milk," by H. Leffmann; "Milk Products," by C. Revis and E. R. Bolton; "Meat and Meat Products," by W. D. Richardson; "Hæmoglobin and its Derivatives," by J. A. Gardner and G. A. Buckmaster; "Albuminoids or Scleroproteins," by J. Alexander; "Fibroids," by W. P. Dreaper. It will be observed that each contribution is dealt with by an expert in his department.

MEETINGS FOR THE WEEK.

- MONDAY, 26th.—Royal Society of Arts, 8. (Cantor Lecture). "The Relation of Industry to Art," by Sir Charles Waldstein, Litt.D., Ph.D.
- TUESDAY, 27th.—Royal Institution, 3. "Animals and Plants under Domestication," by Prof. W. Bateson, F.R.S., &c.
- WEDNESDAY, 28th.—Royal Society of Arts, 8. "Japanese Colour Prints," by Edward F. Strange, R.E. (Hon.).
- THURSDAY, 29th.—Royal Institution, 3. "The Mind of Savage Man," by W. McDougall, F.R.S.
- Society of Dyers and Colourists, 8. "Effects of Mineral Loading upon the Physical Qualities of Hedychium Paper" and "Tests to Determine the Relative Strength and Elasticity of some Natural Fibres," by C. Beadle and H. P. Stevens.
- Royal Society. "Origin of Thermal Ionisation from Carbon," by O. W. Richardson. "X-ray Spectra given by Crystals of Sulphur and Quartz," by W. H. Bragg. "Temperature Variation of the Photo-elastic Effect in Strained Glass," by L. N. G. Filon. "Studies in Brownian Movement—I., Brownian Movement of the Spores of Bacteria," by J. H. Shaxby and E. E. Roberts. "Transmission of Cathode Rays through Matter," by R. Whiddington. "Variation with Temperature of the Specific Heat of Sodium in the Solid and the Liquid State; also a Determination of its Latent Heat of Fusion," by E. Griffiths. "Radiation from a Gas," by G. Green. "Similarity of Motion in relation to the Surface Friction of Fluids," by T. E. Stanton and J. R. Pannell. "Influence of Molecular Constitution and Temperature on Magnetic Susceptibility," by A. E. Oxley. "Boiling-point of Sulphur on the Thermodynamic Scale," by N. Eumorphopoulos.
- FRIDAY, 30th.—Royal Institution, 3. "The Foundations of Diplomacy," by H. Wickham Steed.
- SATURDAY, 31st.—Royal Institution, 3. "Neglected Musical Composers," by Prof. F. Corder.

THE CHEMICAL NEWS

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THE SOLIDIFYING AND MELTING-POINT OF MUTTON TALLOW AND ITS FATTY ACIDS.

By ROBERT MELDRUM.

THE following investigation was undertaken to ascertain the relationship between the melting point and solidifying-point of mutton tallow and its fatty acids. The thermometer bulb method was used for melting-point, and the solidifying-point by Dalican's method, both methods having been previously investigated by the author (CHEM. NEWS., cviii., No. 2813). All the readings are degrees Centigrade. The tallows are fine Australian mutton tallows.

Sample I.—Contains 0·84 per cent Free Fatty Acids.

Solidifying-point + rise.	Rise.	Melting-point.	Difference between s.-p. and m.-p.	Difference between zero and m.-p.
39·8	4·3	48·3	8·5	12·8
40·4	3·0	48·2	7·8	10·9
40·4	4·4	48·4	8·0	12·4
40·6	5·2	48·3	7·7	12·9

Fatty Acids (20·19 per cent KHO to Neutralise).

45·1	1·1	46·8	1·7	2·8
45·4	1·2	46·8	1·4	2·6
45·4	1·2	47·0	1·6	2·8
45·5	1·2	46·9	1·4	2·6

Sample II.—Contains Free Fatty Acids, 1·13 per cent.

41·2	4·8	48·4	7·2	12·0
41·6	5·0	48·0	6·4	11·4
41·4	3·8	48·4	7·0	10·8

Fatty Acids (20·19 per cent KHO to Neutralise).

47·2	1·2	47·6	0·4	1·6
47·2	1·0	47·8	0·6	1·6
47·6	1·0	47·8	0·2	1·2

Sample III.—Contains Free Fatty Acids 0·84 per cent.

44·0	4·4	50·0	6·0	10·4
44·4	5·1	50·0	5·6	10·7
44·3	4·7	50·6	6·3	11·0
44·8	5·4	50·3	5·5	10·9

Fatty Acids (20·19 per cent KHO to Neutralise).

49·2	1·2	49·8	0·6	1·8
49·3	1·1	50·0	0·7	1·8
49·6	1·6	50·0	0·4	2·0
49·5	0·9	49·8	0·3	1·2

Sample IV.—Contains Free Fatty Acids 0·43 per cent.

41·6	4·2	49·0	7·4	11·6
41·7	3·1	48·3	6·6	9·7
42·4	5·2	48·6	6·2	11·4

Sample V.—Beef Tallow.—Contains Free Fatty Acids 0·43.

37·2	3·4	46·6	9·4	12·8
37·8	3·6	46·3	8·5	12·1
37·2	3·6	46·4	9·2	12·8

Fatty Acids (19·48 per cent KHO to Neutralise).

42·8	0·4	43·8	1·0	1·4
42·7	0·3	44·0	1·3	1·6
42·7	0·5	43·6	0·9	1·4

The following table shows the variations in readings on all the samples, indicating the limits of accuracy of methods

used as applied to tallow. It will be noted that beef tallow behaves the same as mutton :—

	Tallow. °C.	Fatty acids. °C.
Solidifying-point + rise	0·8	0·4
Rise	2·2	0·7
Melting-point	0·7	0·4
Difference between solidifying-point and melting-point	1·2	0·4
Difference between lowest T° fat cooled and melting-point	2·0	0·8

The fatty acids, therefore, yield more constant results than the tallows; the latter yielding errors of 50 per cent to 300 per cent greater than the acids. It is clear some erratic conditions are present during the setting of tallow. Such a large variation in the rise shows this more prominently.

Variation in Solidifying-point of Tallow.

This variation in solidifying-point was further investigated. A sample of tallow was selected and melted down in test-tube 7" + 1" at 60° C., fixed in apparatus, and cooled by stirring to 42° C., when thermometer was fixed in centre, 1½ inch from bottom, and allowed to cool.

Thermometer fell to ..	41·7	39·7	39·8	39·3	39·6
Thermometer rose to ..	42·3	41·7	41·7	42·1	42·1
Rise	0·6	2·0	1·9	2·8	2·5

Twenty-four hours after another five tests gave—

Thermometer fell to ..	37·5	37·8	39·1	38·7	38·8
Thermometer rose to ..	40·3	41·1	41·0	40·8	41·4
Rise	2·8	3·3	1·9	2·1	2·6

Variation in rise	2·7
Variation in zero	4·2
Variation in solidifying-point ..	2·0
Average rise	2·2
Average solidifying-point	41·4

The fluctuation in the solidifying-point in the above ten tests is 2·5 times greater than that recorded in the former series of tests. It will be noted the zero to which the temperature falls before rising shows the greatest variation, and it appears it is this factor which governs constancy in the solidifying-point and the "rise." The "zero" is apparently raised or lowered by the stirring, rate of cooling, or other thermal conditions. The following tests show this more clearly. Melted at 60°, cooled by stirring to the indicated temperature, then fixed thermometer.

Cooled to	50	45	40	38	36·2
Thermometer fell to ..	37·4	37·6	37·8	38·7	36·2
Thermometer rose to ..	39·3	39·9	40·3	41·9	40·6
Rise	1·9	2·3	2·5	3·2	4·4

Variation in rise	2·5
Variation in zero	2·5
Variation in solidifying-point ..	2·6
Average rise	2·8
Average solidifying-point	40·4

The tests show that both the setting-point and "rise" increase with the speed of cooling. Theory, therefore, would require that the more rapid a tallow is cooled by means of cold water-baths or cold air, the "rise" and solidifying-point must increase; and, on the other hand, by very slow cooling in warm air or warm water-baths, the "rise" ought to be eliminated and the solidifying-point increased. Such is not the case is seen from the following experiments :—

1. Melted tallow at 60° in test-tube, cooled to 50° by stirring, then fixed in apparatus filled with water at 15°. A rapid and continuous fall takes place, but no "rise" or stationary-point was observed. This was repeated with same result. Theory would require that the latent heat of

crystallisation amounting to 4° ought to produce a "rise" or a "zero" point.

2. Melted at 60° in test-tube, cooled by stirring to 50° , placed in apparatus with water at 50° , and fixed thermometer. One hour in cooling and rising. Thermometer fell to $42^{\circ}3$; rose to $43^{\circ}3$. Rise = 1° . Here there is a tendency to eliminate the "rise" by slow cooling with high solidifying-point, which agrees with theory.

3. 500 grms. melted in beaker at 60° , cooled to 50° by stirring, and thermometer fixed in centre, $1''$ from bottom, and allowed to cool in air at 15° . At $39^{\circ}8$ is quite fluid and transparent, with a layer of solid fat on bottom $\frac{1}{4}$ inch thick. Thermometer falls to $39^{\circ}8$; rose to $44^{\circ}0$. Rise = $4^{\circ}2$. Here the solidifying-point is at maximum with a maximum "rise."

4. 500 grms. as above but cooled to 41° by stirring. Thermometer fell to $40^{\circ}8$; rose to $45^{\circ}2$. Rise = $4^{\circ}4$. It is seen that by varying the conditions of cooling by using air, cold water and hot water jackets, and by using large volumes of tallow, the solidifying varies by $5^{\circ}9$ and the "rise" by $4^{\circ}4$. There is no doubt that the setting-point is affected by stirring, as when stirred the mass becomes semi-solid. No "rise" takes place till the stirring ceases, when there is an immediate rapid "rise."

Variations in Melting-point of Tallow.

A most interesting and important point is that the higher the solidifying-point the more closely does it approach the melting-point. With this particular sample the lowest melting-point obtained was $48^{\circ}4$, or a difference of $3^{\circ}2$ between melting-point and solidifying-point. A great deal of obscurity still persists in chemical and technical literature as regards the change in molecular structure resulting from heating fats, and particularly tallow, at temperatures greatly in excess of the fusing-point. Thus Allen states in his well-known work (vol. ii., p. 21):—"It has been observed that many of the fats solid at ordinary temperatures have at least two *distinct* melting-points. Thus the ordinary tallow of commerce previously melted at a temperature considerably above its fusing-point shows fusion of 95° to 96° F. If carefully remelted at that temperature, cooled, and melting point taken again, it will sometimes be found nearly 20° above the former." Again, he states (vol. ii., p. 22):—"In fatty acids there often is a difference of 3° to 4° C. between the two points, between incipient and perfect fusion." These opinions are still very prevalent amongst technical chemists and analysts. So far as the author's experience and observations are concerned with several hundred samples of tallow, no variation in melting-point has been observed due to temperature of melt or period of heating. The cause is more likely variations in the melting-point method used. So far as the thermometer bulb method is concerned, as applied to tallows and their fatty acids, the results are fairly constant within $0^{\circ}7$ and $0^{\circ}4$ respectively, whatever the heat treatment may be up to 100° C. The variation in melting-point due to thickness of coating of fat on bulb is as follows:—Very thin, $49^{\circ}9$; thick, $48^{\circ}4$; difference, $1^{\circ}5$. Extra thin films on bulb would increase the apparent melting-point considerably, as only a trace of fat would flow to form a drop. The following is a record of the melting-point of this tallow by various methods:—

Melting-point of Tallow by Various Methods.

Thermometer bulb ..	$48^{\circ}6$	$48^{\circ}9$	$49^{\circ}0 = 48^{\circ}4$
Capillary tube ..	$48^{\circ}5$	$49^{\circ}5$	$49^{\circ}0 = 49^{\circ}0$
Test-tube ..	$50^{\circ}5$		$= 50^{\circ}5$

To ascertain what actually takes place during the melting and solidifying of the fat a test-tube, $7'' \times 1''$, half full of the solidified tallow which had been cooled for several hours, was surrounded with water-jacket and heated at the rate of $0^{\circ}5^{\circ}$ per minute during the stirring of both tallow and water in jacket.

45° C.	Opaque soft paste which can be stirred.
48	Opaque thick liquid, easily stirred.
$49^{\circ}5$	Opaque limpid liquid.
$50^{\circ}0$	A trace of opacity present, limpid.
$50^{\circ}5$	Free from opacity, quite transparent.
$50^{\circ}0$	Regains trace of opacity.
$49^{\circ}5$	Opacity increased.
$48^{\circ}0$	Opacity increased and thickness.
$46^{\circ}0$	Very thick and white, semi-liquid.
$44^{\circ}5$	Ceased to stir due to thickness; fixed thermometer; rise commences.
$45^{\circ}7$	Thermometer rose; tallow hard. Rise, $1^{\circ}2$

It will be observed the tallow only completely clarifies at $50^{\circ}5$, and with a drop of $0^{\circ}5^{\circ}$ the opacity reappears. It would therefore appear that the true melting point of the tallow is $50^{\circ}5$, or nearly 2° higher than the thermometer bulb method. This question of incipient and complete fusion or the declaration of two melting-points cannot be maintained, or if admitted there must be present not two but several fusing-points. The actual melting-point must be that at which all trace of opacity disappears and reforms. It appears to the author that the test-tube method of determining melting-points is a very accurate one, as the conditions are under perfect control, and the melting-point based on complete clarification is well defined, and can be confirmed by cooling half a degree. Another important factor is that the fat is obtained in a fluid state, and its viscosity, opacity, and gravity, and other physical properties can be determined at a few points higher or lower than the point of clarification.

The above experiment shows there is absolute agreement between the point at which solidification commences and the actual melting-point— $50^{\circ}5^{\circ}$ C. This relationship between the opacity point and the determined melting-point is a very important one, and is accountable for numerous discrepancies in published melting-points. The following experiment indicates this relationship, which likely holds good for nearly all fats, waxes, and organic compounds. Spermaceti having a melting-point by thermometer bulb method of $45^{\circ}3^{\circ}$ C., and a solidifying-point of $45^{\circ}7^{\circ}$ C. with no "rise" when maintained at 45° C. for one hour is fluid and strongly opaque; at $45^{\circ}7^{\circ}$ C. becomes transparent and free from opacity; cooled to $45^{\circ}5^{\circ}$ C. opacity reappears. So far as this test goes the opacity point is the true melting and solidifying point. To explain, therefore, why tallow and many other solid fats will only solidify several degrees below their opacity point requires further explanation.

Chemical and Physical Changes of Tallow due to Heating.

So far as the author is concerned all the available evidence supports the fact that heating for more or less prolonged periods greatly in excess of the melting point has no disturbing influence on the constancy of either point. The same holds good for rapid and slow cooling, for repeated heating and cooling. If this was not so, wide variations in the melting point would result. The fluctuations in the solidifying-point, therefore, must be due to causes other than these. The changes in molecular state, or chemical constitution, if taking place at all, must happen during the cooling down process or the change must take place at the "zero" point. The chemical change, if present, may result in a combination of the solid and liquid glycerides, or the solid glycerides may undergo partial hydrolysis into mono- and di-stearins. The mechanism of this hypothetical chemical change may be further extended without limit. Chittenden and Smith (*Journ. Chem. Soc.*, xlviii., 508) have recorded stable mixtures of di- and tri-palmitin. It is therefore probable that many double compounds may result of the solid and liquid glycerides by thermal conditions, resulting in a low variable solidifying-point with fluctuating "rises."

The most generally accepted theory as to the melting and solidifying-points of tallow and other fats varying

from the normal is isomerism. Tristearin exists in three isomeric modifications. The theory is as follows:—

- a. Produced by heating tristearin to 74°. Solidifies at 51·7°, melts 52°.
- β. Produced by heating a variety to 52° until it solidifies. Melting-point, 64·2.
- γ. Produced by heating α to 65° or by crystallising stearin from ether. Solidifying-point, 63° C.; melting point, 69·7°.

If the abnormal behaviour of tallow in solidifying is due to this or similar isomeric changes, or to the formation of double compounds, we would expect that by diluting the tallow with a chemically neutral solvent like mineral oil the "rise" resulting from the liberation of heat would decrease with dilution, and erratic ratios between melting-point and solidifying-point would result. Also that some erratic changes would take place by dilution with a fluid animal oil. That such is not the case will be seen from the following results:—

Solidifying-points and Melting-points of Mixtures of Tallow and Mineral Oil (sp. gr. 0·905).

Tallow. Per cent.	Oil. Per cent.	Melting- point.	Solidifying- point + rise.	Rise	Melting-point less solidifying- point.
100	0	50·0	44·2	3·2	5·8
90	10	49·0	44·3	3·2	4·7
80	20	47·1	41·8	3·8	5·3
70	30	46·3	39·2	4·2	7·1
60	40	44·7	36·5	3·5	8·2
50	50	42·7	34·4	4·4	8·3

Solidifying and Melting-points of Mixtures of Tallow and Lard Oil.

100	0	48·0	41·9	4·2	6·1
90	10	47·4	41·6	4·4	5·8
80	20	46·7	40·1	3·8	6·6
70	30	46·0	39·2	4·2	6·8

(Average of four tests for each mixture).

It is conclusive dilution does not affect the "rise" nor the ratio between melting and solidifying-point. It is difficult to reconcile these results with the isomeric theory or chemical theory. Perhaps the data is insufficient for the formulation of any sound hypothesis, but in the course of these and similar researches the author has been strongly impressed with the dynamic factor in crystallisation. The amount crystallised per unit of time in unit mass must affect more or less the uniformity in the "rise" and solidifying-point. The dynamic phase therefore as applied to tripalmitin, tristearin, and other glycerides may be that the speed of crystallisation is slow at the melting-point, and increases to maximum at x degrees lower. This theory would explain the opacity point, and would indicate that point as the true solidifying and melting-point. The three points would then agree together.

The Ratio between the Melting-point of Tallow and its Fatty Acids.

There is a close relationship between the melting-point of tallow and the melting-point and solidifying point of its acids. Thus:—

	1.	2.	3.	4.
Melting-point, tallows ..	48·2	48·0	50·0	46·3
Melting-point, acids ..	47·0	47·8	50·0	44·0
Solidifying-point, acids .	45·4	47·2	49·6	42·7

With more reliable and accurate methods for determining these points, and a clear definition and understanding of the nature of these points and more extensive data, there is indications that these differences would be reduced to a small constant and the "titre" of acids determined directly from melting-point of tallow. It is interesting to note that No. 3 tallow shows little difference in the agreement of its three factors.

The difference between the lowest temperature to which a tallow falls during solidification or its "zero" and its melting-point is apparently a constant approximating 12° or 13°, and in the fatty acids is between 2° to 4°, as will be seen from the following:—

Tallows.

	1.	2.	3.	4.	5.
Melting-point	48·4	48·4	50·6	46·6	48·4
Zero	35·5	36·4	39·3	33·6	36·2
Difference ..	12·9	12·0	11·3	13·0	12·2

Fatty Acids.

	1.	2.	3.	4.	5.
Melting-point	47·0	47·8	50·0	44·0	48·0
Zero	44·2	46·0	48·0	42·2	44·3
Difference ..	2·8	1·8	2·0	1·8	3·7

In all the observations made the tallows, it will be noted, contained free fatty acids, and therefore free glycerin, and whether small amounts of these modify the solidifying-point and is the cause of the low zeros or the erratic "rises," the author is at present investigating.

PASSIVITY.*

By GERHARD C. SCHMIDT.

(Concluded from p. 40).

6. *Proof that a Metal is rendered Active by Diffusion of Hydrogen Ions.—Iron.*

IN order to transform passive iron into the active condition by diffusion of hydrogen, advantage was taken of the discovery of Grave (*loc. cit.*, p. 570) that when hydrogen is liberated at one side of a piece of iron foil, it rapidly diffuses through and alters the e.m.f. The arrangement of the apparatus was as follows:—A and B are two glass troughs, one side of each having been removed and replaced by a thin sheet of iron, Fe. P is a platinum cathode connected with two accumulators. The iron is earthed. The two troughs are filled with dilute potassium

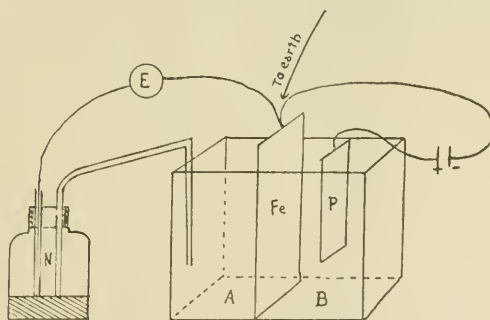


FIG. 1.

hydroxide, which has a slight passivating action. N is the normal electrode. The p.d. between the iron and the normal electrode is measured by means of a sensitive Dolezalek electrometer, E. The alkali renders the metal passive, and it was anticipated that when hydrogen is liberated on one side of the iron the gas will pass through by diffusion and render the iron active. The result of an experiment is shown in Fig. 2, the times being represented as abscissæ and the e.m.f.'s as ordinates. The letters H and O indicate the moment when the liberation of these gases began. The rapidity with which the hydrogen acts

* A Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, November 12, 1913. Experimental Part by W. RATHERT.)

is remarkable. The commencement of its evolution is followed almost instantly by alteration of e.m.f. on the other side.

The investigations did not, however, lead to conclusive results; the iron remained active under all circumstances. The probable reason is that the amount of hydrogen which passes through is too small to counteract the passivating action of the potassium hydroxide. The solution in the trough A was therefore replaced by another electrolyte, chromic acid. The latter is a strong oxidising

metal becomes active. If the evolution of hydrogen is now interrupted (in the second figure B) the metal remains active and dissolves with evolution of hydrogen.

Quantitative investigations showed that more iron is dissolved than corresponds with Faraday's law. This is not surprising, since iron not only goes into solution according to the law in question, but is also acted upon directly by chromic acid. This behaviour is analogous to that of a zinc electrode in sulphuric acid; more zinc is dissolved than corresponds with Faraday's law unless the metal is protected by amalgamation against the direct attack of the acid.

These results, in combination with the above theoretical considerations, are practically conclusive in favour of the hydrogen theory. On the basis of the oxide theory, however, it might be supposed that the metal under the action of the acid becomes coated with oxide

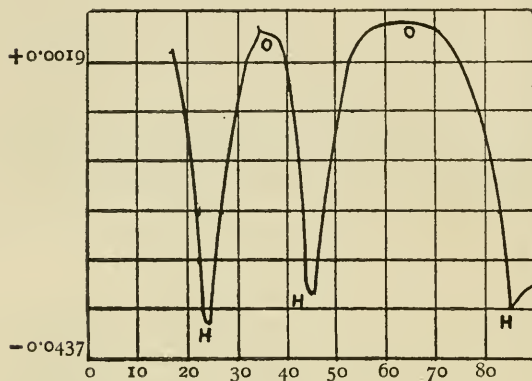


FIG. 2.

and passivating agent as well as an acid. If the hydrogen theory is correct and the iron is highly charged with hydrogen, it ought to be possible so to oppose the two properties of chromic acid that one of them prevails. Preliminary investigations showed that in chromic acid any potential through a wide range can be imparted to iron. The more concentrated the solution the more

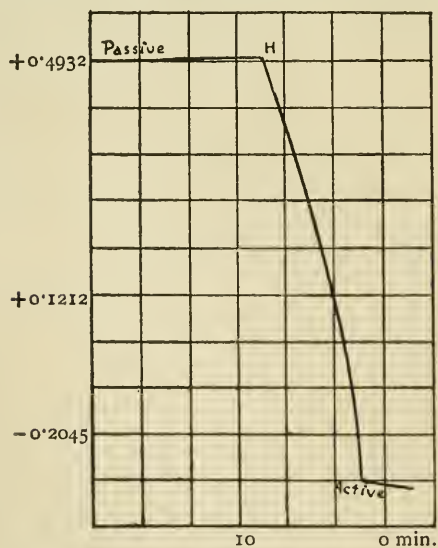


FIG. 3.

positive (more noble) is the potential; the more dilute the solution the less noble is the potential. If an acid is chosen the concentration and oxidising power of which is just sufficient to render the iron passive, it should be possible to render the metal active by hydrogen reaching it by diffusion. The result of such an investigation is represented in Fig. 3, which shows that the iron is at first passive, but the moment that hydrogen begins to be liberated (at H) the potential falls very rapidly and the

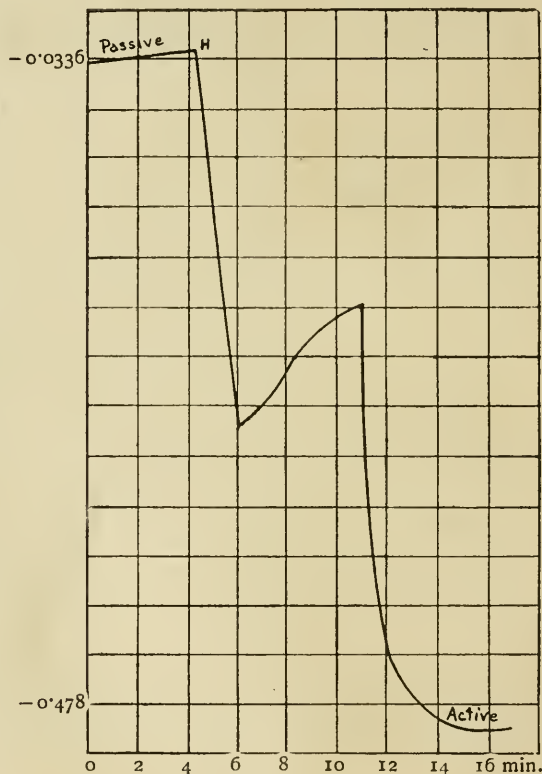


FIG. 4.

which is reduced by the hydrogen so that the electrode again becomes active. To this it might be objected that passive iron remains quite bright in chromic acid. Further, if a layer of oxide is formed at first there would appear to be no reason why this process should not continue. This, however, is not the case, since, as was shown above, when the metal is activated by means of hydrogen it continues active even when the evolution of hydrogen is interrupted. The latter fact can readily be accounted for on the hydrogen theory as follows:—When iron is in process of being dissolved and is passivated at certain points by the chromic acid, local currents are immediately set up and the passive regions again become active under the influence of the liberated hydrogen.

Moreover, according to the oxide theory, iron in chromic acid should be rendered active by rupture of the surface film by scratching, which is not the case. Further, an oxide of definite composition, such as is presumably

postulated in this case, should show a definite potential, whilst it was found that iron in chromic acid shows all possible potentials, depending on the concentration of the acid.

All these results and arguments constitute so powerful support to the hydrogen theory as to put its validity practically beyond question, more particularly as the most delicate methods have failed to detect a trace of the hypothetical oxide.

7. Chromium.

The successful results obtained in the activation of passive iron by diffusing hydrogen induced me to make analogous experiments with chromium. The metal was electrolytically deposited on thin sheets of iron or steel. After about fourteen days the initially active metal became

evolution of hydrogen, and it continued active when the cathodic polarisation was interrupted. Of the other experiments, which gave analogous results, only one is quoted, as it shows the rapidity of action of the hydrogen.

TABLE II.

(Chromium deposited on a Steel Foil 0.08 mm. thick.
Electrolyte 0.1N H_2SO_4).

Potential.	Time. Min.	Evolution of Gas.
-0.1976	0	
-0.2232	3	
-0.2488	6	
-0.5310	6.5	Hydrogen
-0.5310	7.5	
-0.5246	8.5	
-0.5112	13.5	

The results are represented in Fig. 5. The electrode was originally passive; within half a minute of the commencement of the evolution of hydrogen it became active and began to dissolve with rapid evolution of gas. The dissolution continued after interruption of the cathodic polarisation till all the chromium had disappeared.

Conclusion.

In the foregoing a series of observations have been described which in our opinion cannot be explained on the oxide theory, but are in best accord with the hydrogen theory. The views of the author on the phenomenon of passivity have already being briefly described by Grave. Just as water or other liquids do not boil, even when their vapour pressure is equal to that of the superincumbent pressure, unless a catalyst such as air is present, so the metals which can be passivated dissolve *rapidly* only in the presence of a catalyst. The most important of such catalysts is hydrogen, since it is dissolved readily and in large amounts by metals. Whether other gases are also catalytically active cannot at present be stated, since they are only absorbed to a very small extent by metals. Just as relatively small amounts of air initiate rapid evaporation in large quantities of liquid, so a small quantity of hydrogen can activate large amounts of iron, nickel, and chromium. It might be supposed that the hydrogen, like air in the case of boiling, forms a nucleus round which the ions of metal collect. Further investigation must decide whether this hypothesis is in accord with the facts.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

THE PROGRESS OF THE ELECTRO-METALLURGICAL INDUSTRY.

Some very interesting facts with regard to the progress of modern science in electro-chemistry and electro-metallurgy have just been established by M. Gall, the new President of the Society of Civil Engineers. These two forces have been recently placed at the disposal of technical labour at a price hitherto unknown for metals or alloy, the demands for which increase day by day. M. Gall, on taking the chair at the recent Meeting of Civil Engineers, reviewed the principal industries, electro-chemistry and electro-metallurgy. He drew attention to the remarkable development of these two scientific discoveries during the last thirty years. The electrolytic refining of copper only produced at first 20 tons of electrolytic-copper per day; that is to say, 4 per cent on the total consumption. In 1910, thirty-eight factories refined 469,000 tons of copper, representing 55 per cent on the entire production. "J. B. Dumas," said M. Gall, "has preserved for us the souvenir (in an anecdote of Faraday) of the emotion felt by that great Professor of Chemistry when he saw the first globule of alkaline metal

passive—probably owing to gradual loss of hydrogen. The experiments were made as described above. The results are given in the accompanying table and are represented graphically in Fig. 4.

TABLE I.

(Chromium deposited on Steel and allowed to stand
Fourteen Days in 0.1N Sulphuric Acid exposed to
the Air).

Potential.	Time. Min.	Evolution of Gas.
-0.0336	0	
-0.0262	4	
-0.3059	6	Hydrogen
-0.2909	7	"
-0.2321	9	"
-0.2174	11	"
-0.4310	12	"
-0.4530	13	"
-0.4780	14	"

The chromium electrode was at first passive. Under the influence of the diffusing hydrogen the potential fell at first rapidly, then more gradually till it reached a value of -0.2174 volt and finally fell within a minute to -0.4310 volt. The electrode was then active, as shown by the fact that it began to dissolve with a vigorous

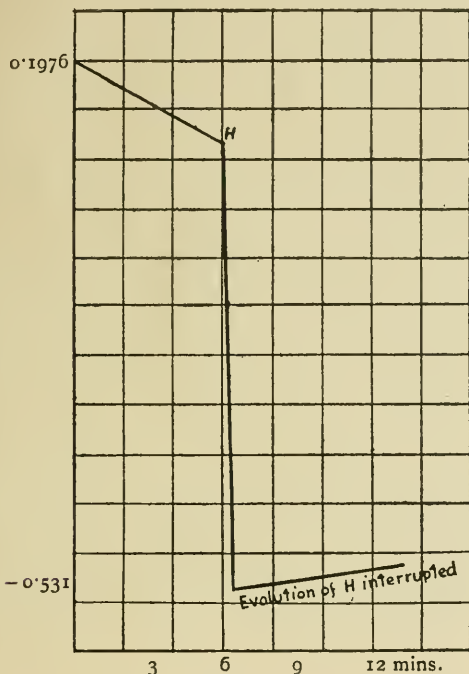


FIG. 5.

appear, by the influence of the pile that the hand of man had ever isolated." "Experience capitale" is the title given by Davy to this experiment on the register preserved at the Royal Society. The fabrication of soda since these researches has developed considerably. As to aluminium discovered by Henri Sainte-Claire Deville, the entire production is more than 50,000 a year, and the production in France alone is more than 15,000 tons. The uses of the electric furnace are numerous. "Ferro-silicon" and the "ferro-chromium" are manufactured by millions of tons. The production of electric steel is more than 120,000 tons a year. Lastly, carbide of calcium is an important production of the electric furnace. In the whole world there are more than 300,000 tons of carbide of calcium manufactured yearly, and out of that France manufactures 36,000 tons. A recent and very important application of the electric furnace is the production of nitrogenous manure, drawn from atmospheric nitrogen. Sir W. Crookes pointed out that the increase in the white races entails an augmentation of many necessary cereals, which must be extensively cultivated to satisfy the demand. It is proved that Germany (which only produces two-thirds of the corn necessary for its consumption) could increase the cultivation 4,000,000 tons, by using 130 kilogrms. of manure per hectare. Statistics go to prove that during the present century the beds of nitre in the mines of Chili will become exhausted—according to some in the year 1940 and to others in the year 2032. The production direct of nitrates is to-day an accomplished fact. At the present moment 160,000 tons of calcium cyanamide are manufactured, which corresponds to 30,000 tons of nitrogen. Other methods furnish about 160,000 tons of nitrate of lime, and this is only the commencement. For the whole of France the statistics value the force of industrial motors at 3,144,000 horse-power, and of those of railways and tramways at 10,309,000 horse-power. We arrive thus at a necessary force of 50 milliards, 700 millions of horse-power hours. The hydro-electric force of France is, according to M. Gall, equal to a tenth of this amount. It could immediately be increased 50 per cent by the utilisation of two electromotive forces, that of the Rhone and that of the Durance. The utilisation of each of these forces corresponds to the discovery of coal-beds producing, one 1,800,000 tons, the other 80,000 tons of coal a year.

TO RECEIVE THE SIGNALS OF THE T.S.F.

M. Bigourdan, astronomer of the "Observatoire," presented to the Academy a paper from MM. Tauleigne, Ducretet, and Roger on a new system for registering on a Morse-receiver wireless telegraphy signals, which are generally transmitted by telephone. This method comprises a "detector electrolytique à réglage," combined with the use of a magnetic polarising relay. The three experimentists have been able to register signals at a distance of 150 and 170 kilometres by means of a rod 12 metres long, held to a height of 12 metres from the ground.

Action of Alkaline Sulphites on Acetylenic Acids and their Ether Salts.—E. Lasausse.—Neutral alkaline sulphites act on free phenyl propionic acid to give the neutral salt of a β -sulphocinnamate. Sodium disulphite reacts with methyl phenylpropionate to give the cinnamate of methyl monosulphonate of sodium and the phenylpropionate of methyl disulphonate of sodium. Methyl amylpropionate fixes 2 molecules of sodium disulphite with formation of the saturated disulphonic derivative, $C_5H_{11}-C_2H_2(SO_3Na)_2-CO_2CH_3$. Thus it is possible to attach 1 or 2 molecules of an alkaline disulphite to the salts and ether salts of acetylenic acids of general formula $R-C\equiv C-CO_2H$. In the first case the product is the alkaline salt of a monosulphonic acid with an ethylene bond; and in the second case the alkaline salt of a saturated disulphonic acid.—*Bull. Soc. Chim. de France*, 1913, No. 18-19.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 18th, 1913.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

REFERENCE was made to the death, on December 4, 1913, of Mr. Christer Peter Sandberg, of Westminster, who was elected a Fellow on March 3, 1870.

Messrs. H. F. Tayler, A. O. Blackhurst, V. Lefebure, C. J. Dickenson Gair were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Ethelbert William Blair, B.Sc., 70, Fountayne Road, Stoke Newington, N.; Richard Charles Denington, 69, Dover Road, S. Wanstead, N.E.; John Garth, 170, St. Thomas's Road, Preston; Ivan Richard Gibbs, B.A., University Hall, 3, Moors' Gardens, Chelsea, S.W.; Theophilus Harper, 39, Camden Street, Belfast; William Pawson Robson, B.A., Ph.D., 78, Rolland Street, Cape Town; Chandra Bhusan Roy, M.A., Patna College, Moradpore, P.O., Bankipore; M. R. Viswanatha Tyer, 50, Prem Chand Bural Street, Bow-Bazar, Calcutta.

The PRESIDENT announced that, at the request of the International Committee on Physico-Chemical Nomenclature, the Council invited criticism of the symbols recently suggested by the International Association of Chemical Societies. For these symbols Fellows were referred to the *Proc. Chem. Soc.*, xxix., 333 (see also *CHEM. NEWS*, cviii., 293), and were requested to forward any suggestions to Prof. A. Findlay, University College, Aberystwyth, before February 28, 1914.

The announcement was also made that, in order to give Fellows more frequent opportunity of meeting informally, the Rooms of the Society would be opened on January 15, 1914, at 8 p.m., when the President and Council would be glad to meet the Fellows of the Society. Smoking will be permitted, and light refreshments will be provided. Fellows were also invited to exhibit apparatus or specimens of interest and to show experiments; those willing to do so were requested to communicate with the Secretaries before the Monday previous to the Meeting.

Of the following papers, those marked * were read:—

*330. "*Absorption of Gases by Celluloid*." By VICTOR LEFEBURE.

An absorption of gases by celluloids of a magnitude comparable with the sorption of gases by some charcoals has been observed by the author, and the chief points already established are as follows.

The effect is reversible. It is not chemical, in that no compound with a very low or with a moderately large dissociation pressure is formed, assuming that such compounds would not form solid solutions with the celluloid. It is common to all the kinds of celluloid examined, but almost vanishes when a precipitate of celluloid constituents is substituted for film celluloid. The property is recovered by the refilmed precipitate. Again, it is not exhibited by the two chief constituents of the celluloid, camphor and nitrocellulose. Finally, the effect increases with lowering of temperature and raising of pressure, and in general nature resembles a case of sorption.

The quantitative experiments which have been carried out are concerned with time, diffusion, and equilibrium. The equilibrium experiments yield isotherms of the type given by previously examined sorption effects. The time experiments, yielding curves representing rates of sorption, indicate the possibility of a development of surface within the celluloid mass, and probably near to the external visible surface. The diffusion experiments have merely established the fact of diffusion through films.

DISCUSSION.

Prof. DONNAN wished to congratulate the author on the excellent way he had carried out the work. He thought that Mr. Lefebure's paper was the first investigation of that nature on a semi-solid colloidal film.

The great rapidity of the initial absorption of the carbon dioxide by the celluloid, and the fact that the speed of absorption increased much more rapidly (per unit of weight of celluloid) than the increase of apparent (external) surface of the film, showed that in the mass of the celluloid or perhaps in the neighbourhood of the surface there was a very fine-grained macro-porosity into which the gas could rapidly penetrate and be adsorbed. Diffusion of the gas into or through molecular pores was simply what one called solution, and, so far as one knew, solution phenomena in semi-solid gels were relatively slow at the temperatures at which Mr. Lefebure had worked.

Solution and diffusion in the ordinary sense probably also occurred in the case of the celluloid films, and accounted for the later portions of the velocity curves.

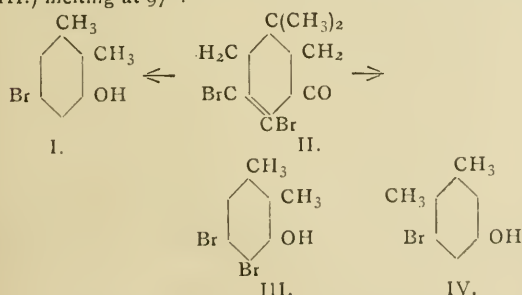
Very little was known concerning the macro-heterogeneity of the camphor-nitrocellulose system, but Mr. Lefebure's work was an important contribution to the subject.

Mr. W. P. DREAPER pointed out that it was possible to vary the porosity of structureless cellulose filaments within wide limits by varying the strain under which they were dried at the time of manufacture. It might be possible to utilise this in determining the effect of porosity on the adsorption of gases by this material, and in this way confirm, or otherwise, some of the conclusions arrived at by the author. From this point of view it was strange that the precipitated cellulose gave a lower result, as it would certainly expose a considerable surface to the gas, and be relatively porous.

*331. "Aromatic Compounds obtained from the Hydro-aromatic Series. Part III. Bromoxylenols from Dimethyl-dihydroresorcin." By ARTHUR WILLIAM CROSSLEY and NORA RENOUF.

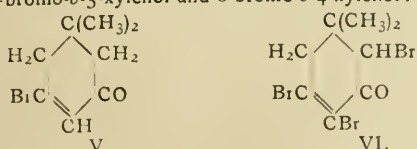
In continuation of the work, of which a preliminary note has appeared (*Proc.*, 1912, xxviii., 332), the following rearrangements of hydroaromatic to aromatic substances have been established:—

1. Under the influence of alcoholic potassium hydroxide dibromodimethylcyclohexenone (II.) gives 5-bromo-*o*-3-xynol (I.) melting at 84° and 4:5-dibromo-*o*-3-xynol (III.) melting at 97°:—



2. Heat causes the elimination of hydrogen bromide from dibromodimethylcyclohexenone, with production of 5-bromo-*o*-3-xynol and 6-bromo-*o*-4-xynol (IV.) melting at 103°.

3. Bromine acts on bromodimethylcyclohexenone (V.) to yield, in the first place, a mixture of hydroaromatic substances, which on heating loses hydrogen bromide to give 5-bromo-*o*-3-xynol and 6-bromo-*o*-4-xynol:—



4. Tribromodimethylcyclohexenone (VI.) under the influence of heat or alcoholic potassium hydroxide yields 4:5-dibromo-*o*-3-xynol and other bromoxylenols, which, up to the present, it has not been found possible to separate in a pure state.

*332. "The Equilibrium of Dilute Hydrochloric Acid and Gelatin." By HENRY RICHARDSON PROCTOR.

The author referred to a previous paper (*Koll. Chem. Beihefte*, 1911, ii., 243), in which it was shown that the swelling of gelatin in dilute acids, and the amount of acid absorbed, can be explained on the current hypothesis of chemical affinity and osmotic pressure. Precise mathematical expressions for these relations were now given, and it was shown that the two basic affinity-constants of gelatin being known, together with molecular weight, and a small correction for original alkalinity, its whole behaviour with regard to dilute acids can be prognosticated. The mathematical relations are quite general and applicable to other amphoteric proteins and other acids and their salts, and all the concentrations in the jelly were shown to be mathematical functions of the concentrations of the equilibrium-acid only, and not dependent on the chemical character of the protein. Gelatin appears to be diacid as a base, with hydrolysis constants $K_1 = 0.0013$, $K_2 = 1.05$, and an approximate molecular weight of 839, leading to the formula $\text{C}_{35}\text{H}_{57}\text{O}_{13}\text{N}_{11}$.

Some difficulties in the applications of the electrometric method to colloidal equilibria were mentioned, and it was pointed out that in consequence of surface-potentials the ionic concentrations measured with the concentration cell in colloid solutions are not those of the colloid solution itself, but of the acid or other solution with which it would be in equilibrium. Suggestions were made with regard to the probable colloidal structure of protein jellies and solution. A graphic geometrical method was described for dealing with all such equilibria as depend on the "equality of products."

DISCUSSION.

Prof. DONNAN thought that the methods of investigation employed by Prof. Proctor were the right ones, and would lead him eventually to a solution of his problems.

He observed that the author inclined to the view taken by Arrhenius in his work on immunity, namely, to treat the phenomena as cases of molecular equilibrium, without much reference to adsorption and colloidal aggregation and disaggregation.

Nevertheless in his (Prof. Donnan's) opinion both series of phenomena occurred, and must be taken into account.

He would refer Prof. Proctor to the work of two Italian investigators, an account of which was to be found in the "Nernst Festschrift."

*333. "Researches on Residual Affinity and Coordination. Part I. Metallic Acetylacetonates and their Absorption Spectra." By GILBERT T. MORGAN and HENRY WEBSTER MOSS.

An examination of the absorption spectra of fourteen metallic acetylacetonates in alcoholic solution showed that, with the exception of the chromium compound, all these substances exhibit a well-marked absorption band in the ultra-violet.

Chromic acetylacetonate showed a band of this character, but in addition a well-defined band toward the red end, probably due to the metallic radicle. Comparative experiments were made on the volatility of scandium and thorium acetylacetonates under the ordinary and under 8–10 mm. pressure.

*334. "Ionisation and the Law of Mass Action. Part II. The Osmotic Data in Relation to Combined Water." By WILLIAM ROBERT BOUSFIELD.

It was shown by reference to the figures for sucrose that the osmotic data can be brought into accurate conformity with the gas equation by taking account of the combined water. The osmotic pressure equation, vapour-pressure equation, and freezing-point equations then present themselves in the following forms:—

$$\begin{array}{ll} \text{O.P. equation } P/R'\theta (h-n)=i \\ \text{V.P. } \rho \delta p/p (h-n)=i \\ \text{F.P. } \Delta/F' (h-n)=i, \end{array}$$

where h is the total number of molecules of water per mol. of solute and n is the number of combined molecules of water per mol. of solute.

DISCUSSION.

Prof. DONNAN thought that there were some misconceptions in that paper. There was absolutely no *a priori* reason to "expect" the equation $PV = RT$ to hold for more concentrated solutions.

The general theoretical osmotic equation for solutions of any strength was now well known. If, however, there was practically no volume or energy-change on solution, this equation, as was well known, reduced to a simple form for solutions of any concentration. If solvation occurred, then, of course, in relatively concentrated solutions allowance had to be made for it.

The calculations of Mr. Bousfield might serve to show that after this allowance had been made aqueous solutions of sucrose of very considerable concentration approximated to the "simple" behaviour referred to above. In Prof. Donnan's opinion this suggestion had been made by previous authors.

335. "Chemical Examination of Sarsaparilla Root." By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY.

The material used for the present investigation consisted of grey Jamaica sarsaparilla root, such as is recognised by the British Pharmacopoeia.

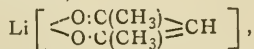
The root was found to contain a small amount of an enzyme, which slowly hydrolysed amygdalin.

An alcoholic extract of the root yielded, besides a little essential oil, the following definite compounds:—(i.) a crystalline glucoside, sarsasaponin, $C_{44}H_{76}O_{20} \cdot 7H_2O$, which, on hydrolysis, is resolved into sarsapogenin, $C_{26}H_{42}O_3$, and dextrose; (ii.) sitosterol-*d*-glucoside (phytosterolin), $C_{33}H_{56}O_6$; (iii.) sitosterol, $C_{27}H_{46}O$; (iv.) stigmasterol, $C_{30}H_{50}O$; (v.) a new crystalline dicarboxylic acid, *sarsapic acid*, $C_6H_4O_6$ (m.p. 305°), which yields a dimethyl ester, $C_8H_8O_6$, melting at 121° ; (vi.) dextrose; (vii.) a mixture of fatty acids, consisting of palmitic, stearic, behenic, oleic, and linolic acids. The alcoholic extract contained, furthermore, a small quantity of a substance which possessed the characters of cetyl-*d*-glucoside, and a considerable quantity of potassium nitrate was also present. The amount of resinous material was equivalent to about 1.25 per cent of the weight of root employed.

It has now been shown that Jamaica sarsaparilla root contains but one definite saponin glucoside, namely, sarsasaponin, and it is considered probable that the "parillin" of previous investigators was a mixture of sarsasaponin and a phytosterolin. It has also been definitely ascertained that the so-called "smilacin" ("smilasaponin" of v. Schulz) is not a homogeneous substance, but contains a relatively small proportion of sarsasaponin, together with amorphous material.

336. "Metallic Derivatives of Acetylacetone and Acetyl Mesityl Oxide." (Preliminary Note.) By GILBERT THOMAS MORGAN and HENRY WEBSTER MOSS.

Series 1.—With the exception of copper, the metals of the first vertical series of the periodic classification yield somewhat unstable derivatives with acetylacetone. Lithium acetylacetone,—



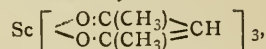
a colourless, crystalline mass, decomposed when dissolved in the ordinary organic media, the solutions assuming a yellow colour.

Caesium acetylacetone, a colourless, crystalline mass soluble in water or alcohol, was much less stable than the preceding compound. Silver acetylacetone, obtained as a white, crystalline precipitate, rapidly darkened on exposure, with liberation of silver; it is sparingly soluble in

water; the solution rapidly deposited a silver mirror. The blue copper acetylacetone yielded a green additive compound with quinoline.

Series 2.—Zinc acetylacetone, formerly described as a yellow substance, was obtained in colourless, acicular prisms, soluble in hot water or alcohol. Its cadmium analogue was much less soluble.

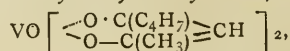
Series 3.—Scandium acetylacetone,—



melting after sublimation at $187-187.5^\circ$, crystallised from benzene in colourless, tabular prisms, or from chloroform in square plates. It was prepared by the interaction of scandium nitrate, acetylacetone, and ammonia. The molecular weight determined by the ebullioscopic method corresponded with the above formula.

Comparative experiments made with yttrium, erbium, and thorium indicate that the acetylacetones of scandium and yttrium (the two rare earth metals of least atomic weight) do not under similar experimental conditions yield additive ammonia compounds comparable with those obtained from acetylacetones of the rare earth metals of higher atomic weight.

Series 5.—Vanadyl acetyl mesityl oxide,—

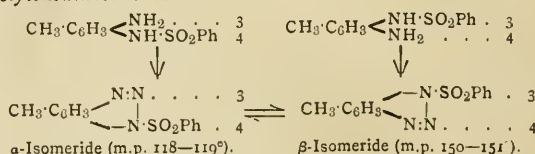


prepared by the interaction of vanadyl sulphate, acetyl mesityl oxide, and ammonia, crystallised from light petroleum in grass-green leaflets.

Other metallic derivatives of acetyl mesityl oxide are under examination; they are characterised by their ready solubility in organic solvents, including light petroleum.

337. "Constitution of the Ortho-diazoimines. Part IV. Isomeric Benzenesulphonyl-3:4-tolylenediazoimides." By GILBERT THOMAS MORGAN and GODFREY EDWARD SCHARFF.

3-Nitro-*p*-toluidine and 4-nitro-*m*-toluidine (m.p. $111-112^\circ$), the latter base prepared from either *m*-cresol, *m* toluidine, or diacetyl-2:5-tolylenediamine, were converted respectively into the isomeric 4-benzenesulphonyl-3:4-tolylenediamine and 3-benzenesulphonyl-3:4-tolylenediamine. These acylated ortho-diazoimines yielded the corresponding isomeric diazoimides, 4-benzenesulphonyl-3:4-tolylenediazoimide and 3-benzenesulphonyl-3:4-tolylenediazoimide.



The α -isomeride is a more soluble, labile modification, which on prolonged boiling in solution changes almost completely into the less fusible, more sparingly soluble, stable β -isomeride.

338. "Organic Derivatives of Silicon. Part XXI. The Condensation Products of Diphenylsilicanediol." By FREDERIC STANLEY KIPPING and ROBERT ROBISON.

The study of the four condensation products of diphenylsilicanediol previously described (Kipping, *Trans.*, 1912, ci., 2125) has been continued in order to ascertain the conditions under which each is formed.

The results seem to show that diphenylsilicane, SiPh_2O , the analogue of benzophenone, is not produced by the dehydration of diphenylsilicanediol, and that the closed-chain compound,—



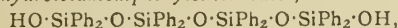
is not formed by the dehydration of anhydrosilicanediol.

In the presence of piperidine, solutions of diphenyl-

silicanediol and of anhydrobisdiphenylsilicanediol both give tetra-anhydrotetrakisdiphenylsilicanediol, and probably also some trianhydrotrisidiphenylsilicanediol.

Dianhydrotrisidiphenylsilicanediol may be obtained by carefully hydrolysing trianhydrotrisidiphenylsilicanediol with alkali in ethereal acetone solution; it is very rapidly converted into trianhydrotrisidiphenylsilicanediol in methyl-alcoholic solution in the presence of a little hydrochloric acid. Trianhydrotrisidiphenylsilicanediol is also formed when anhydrobisdiphenylsilicanediol is treated with a methyl-alcoholic solution of hydrochloric acid, but the reaction takes place slowly.

Trianhydrotetakisidiphenylsilicanediol,—



the most complex open-chain condensation product so far obtained, may be prepared by very cautiously hydrolysing the tetra-anhydro-derivative with sodium hydroxide in chloroform solution; it melts at 127°, and is easily converted into the tetra-anhydro-derivative by traces of sodium hydroxide in alcoholic solution.

339. "*The Absorption Spectra of Sulphurous Acids and Sulphites*." (Preliminary Note.) By ROBERT WRIGHT.

While comparing the absorption spectra of various acids with their salts, it was found that whilst the absorption of sulphurous acid is characterised by a band in the ultra-violet, the sodium salt exhibits only general absorption. It is thought that this is most probably due to a difference in structure between the acid and its salt, additional evidence in favour of this view being the fact that whilst the acid has the properties of a moderately strong acid, its salt suffers hydrolysis in aqueous solution, thus behaving like a derivative of a weak acid.

A parallel case is to be found in the behaviour of chromic acid and its salts, where a strong acid differs in visible colour from its salts, the latter also being hydrolysable.

(To be continued).

NOTICES OF BOOKS.

Researches in Magneto-optics. By P. ZEEMAN, Sc.D., Ph.D., D.Sc. London: Macmillan and Co., Ltd. 1913.

THIS monograph contains a very stimulating account of the author's remarkable work in magneto-optics, and since highly technical details are omitted as far as possible it may be read by the educated general public with as much interest as by the scientific man. The author's manuscript has been translated from the Dutch by Miss J. D. van der Waals. The arrangement of the text closely follows the historical development of the subject, and the author's first paper on "The Influence of Magnetism on the Nature of the Light Emitted by a Substance," laid before the Academy of Sciences at Amsterdam in 1896, is reprinted almost in full. The apparatus employed in modern spectroscopic work is admirably described, and the investigations of other workers in the same sphere are fully described. Some new results are published in the monograph for the first time; for example, the determination of the ratio of the number of emitting atoms to the whole number present in the flame, and in the last chapter some account is given of Sir J. J. Thomson's work on the constitution of the atom.

General Chemistry Laboratory Manual. By J. C. BLAKE, Ph.D. New York: The Macmillan Co. 1913.

THIS book of practical chemistry is intended to be used as a laboratory companion to the author's "General Chemistry, Theoretical and Applied," and the numbering of the chapters and sections is the same as in the text-book. Methods of preparing many elements and inorganic compounds are described, and a short course of analytical work is included, besides a rather sketchy outline of

practical work in applied chemistry, including very simple experiments with fuels, soils, waters, &c. The book will no doubt be found convenient by those who are using the text-book or attending the author's lectures at the Agricultural and Mechanical College of Texas, but it hardly presents sufficient novelty or special merit to suggest that its more extended use could be warmly recommended.

Calico Engraving. By WILLIAM BLACKWOOD. London: Charles Griffin and Co., Ltd. 1913.

THIS book is based upon the lectures delivered by the author at the Royal Technical College, Glasgow, on engraving designs for calico, but in preparation for the press the lectures have been very much extended, and both skilled designers and students will find the book most instructive. The author enters fully into technicalities, and machinery of many different types is thoroughly explained and illustrated. Valuable hints are given for the benefit of hand engravers, and engraving for paper stainers is also discussed. Electroplating is very briefly treated, and if the theoretical explanations are somewhat curtailed it is quite possible that they are sufficient for the purpose for which they are intended.

Practical Chemistry. By the late J. CAMPBELL BROWN, D.Sc., LL.D. Sixth Edition. Edited by GUY D. BENGOUGH, M.A., D.Sc. London: J. and A. Churchill. 1913.

THIS very useful book contains a concise summary of the chief reactions employed in analytical work, and includes a good deal of matter not usually to be found in similar books of the same size. Thus the reactions of some of the rarer elements are given, also those of many organic bases and of some neutral organic substances which are commonly used in the laboratory. The analysis of gases is also shortly treated. A great deal of information is compressed into the book, but for the use of students the directions may very possibly be found to be somewhat too concise. For example, unless used to gas analysis the student might be somewhat at a loss when told merely to "separate the gases into two groups by a solution of sodium hydrate." For practising analytical chemists, however, the book can be recommended as containing clear and accurate descriptions of experimental work.

Chemistry, Inorganic and Organic. With Experiments. By CHARLES LOUDON BLOXAM. Tenth Edition. Rewritten and Revised by ARTHUR G. BLOXAM, F.I.C., and S. JUDD LEWIS, D.Sc., F.I.C. London: J. and A. Churchill. 1913.

FOR nearly fifty years Bloxam's "Chemistry" has enjoyed the well deserved reputation of being the most compendious work on chemistry in a single volume, and those who have had occasion to use it will probably not need to be reminded how often they have found in it information not to be obtained even from larger and more detailed treatises. The original author showed remarkable skill in selecting his material, and this feature is as noticeable in the last as in the first edition. Very many changes have had to be made in the tenth edition. Thus all the earlier chapters have been recast, and throughout the book the Periodic System of classification has been followed more closely than before. The division of the text into numbered paragraphs has been dropped, and the appendix on applied chemistry is omitted.

The Sugars and their Simple Derivatives. By JOHN E. MACKENZIE, D.Sc., Ph.D. London: Gurney and Jackson. 1913.

THIS book is based upon a course of lectures delivered by the author at Birkbeck College, London, and afterwards at the University of Edinburgh. Many students who were interested in technological chemistry attended these lectures, and for their benefit stress was laid upon those

points in the chemistry of the sugars which are of special importance in the sugar and brewing industries and in medicine. At the same time the book gives a really useful introduction to the subject for students of pure chemistry, and questions of configuration, &c., are so clearly treated that candidates for examinations will find it a valuable summary. The first part of the book contains some account of the production and manufacture of cane-sugar, and subsequently the properties and constitution of the individual sugars are described. Fermentation and metabolism are shortly dealt with in later chapters.

Principles and Processes of Metal Plate Work. By EDWIN G. BARRETT. London: Crosby Lockwood and Son. 1914.

THIS book has been compiled to meet the requirements of candidates for the examination in metal plate work of the City and Guilds of London Institute, and it will be found to fulfil its purpose admirably. The author has carefully studied the examiners' criticisms of the average candidate's work, and has paid special attention to those points in which particular weakness is usually displayed. Thus methods of performing numerical calculations are very carefully explained, and many mensuration formulæ are given. Model answers are also provided, and the syllabus of the examination in metal plate work and also recent questions are reproduced. The book will be of service to metal plate workers other than those entering for the examination, and if they wish to acquire some knowledge of the theory of such work they cannot do better than to get a copy of it.

The London Matriculation Directory. No. 65, September, 1913. London: University Tutorial Press, Ltd.

No. 65 of the "Matriculation Directories" closely resembles its predecessors, and contains the usual articles on textbooks, details of the classes of the University Correspondence College, and hints to intending candidates for the examination. Many of the papers sent in September, 1913, are reproduced in it with full solutions and comments upon them. Although on the whole a wise choice is made of the papers for reproduction, and they deal with those subjects which are most popular in the examination, it seems probable that some students would be glad to see some of the others, such as those on Ancient History, Geology, or Zoology, even if it were not worth while to prepare answers to them.

London University Guide, 1914. London: University Correspondence College.

THIS guide contains a full almanac and calendar for 1914, with the regulations of the more important examinations. Details of the classes and the fees of the University Correspondence College are also given, and the guide contains some articles on text books and an interesting short history of the University of London and account of its constitution. Recent changes in the regulations are pointed out, and the guide is an almost indispensable possession for the intending candidate for an examination of London University.

The Burroughs Wellcome Photographic Exposure Record and Diary for 1914.

CONTAINS much useful information for photographers. The "Record of Negative Exposures" is invaluable for any who care to introduce "method" into their work, and the Exposure Calculator is an ingeniously designed apparatus by help of which the correct exposure can be calculated. Some very good prints are included in the book; one of Mr. H. C. Ponting, F.R.G.S., at work in his dark room at Cape Evans, speaks well for the value of the comparatively new developer Rytol. There is a good diary and memorandum book included, and the book is not too bulky for the pocket or the camera case.

CORRESPONDENCE.

SPECIFIC GRAVITY DIFFERENCES.

To the Editor of the Chemical News.

SIR,—It is a curious fact, which I have never seen noted elsewhere, that if the six cases which I can readily call to mind and find figures for in which there are three varieties of a substance, in four cases the difference in the specific gravity between the first two is equal to the difference between the second two:—

1. {	Diamond	3.514	←	1.01
	Graphite	2.5	←	1.05
	Amorphous carbon ..	1.45		
2. {	Grey arsenic	5.527	←	1.0
	Black arsenic	4.7	←	1.0
	Yellow arsenic	3.7		
3. {	Rhombic tin	7.25	←	0.70
	Tetragonal tin	6.55	←	0.75
	Grey tin	5.8		
4. {	Aragonite	2.93	←	0.21
	Calcite	2.72	←	0.20
	Vaterite	2.52		

It is hard to see that there can be any significance attached to this, but the mathematical odds against it being entirely due to chance are very great. Moreover, in the case of one of the exceptions, silica, the second difference is almost an exact multiple of the first.

Quartz	2.67	←	0.34
Tridymite	2.33	←	0.11 (= 3 × 0.11)
Vitreous	2.22		

In the last case, that of sulphur, no such relation is evident, the difference between rhombic and monoclinic sulphur being 0.13, and that between monoclinic and amorphous sulphur 0.02.—I am, &c.,

EDGAR B. WASTELL.

51, Gillott Road, Birmingham.

INSTITUTE OF CHEMISTRY CONFERENCE.

To the Editor of the Chemical News.

SIR,—With your permission I should like to reply to the letter of Mr. E. A. Lewis, which was published in your issue of the 2nd January.

The last part of his letter raises an important point of general interest.

It is essential that the chemical profession should include all persons who are engaged in teaching the principles of chemistry, or in applying those principles towards the attainment of practical results. These persons only can claim to be professional men in the sense in which that term is usually accepted. The profession should not include those persons whose interests are directly commercial.

Any profession worthy of the name should consist of a united body of men, but true professional unity is not attained by setting up, at the outset, educational barriers of a more or less artificial kind.

This mistake, however, has been made in the case of the chemical profession, with the result that the profession has been divided against itself, the status of technical chemists has been lowered, their professional interests endangered, and the technical interests for which the profession stands have suffered.

It is unnecessary to insist on the national importance of applied chemistry. The fact that universities and technical colleges give a large amount of time and money in training students in the principles of chemistry is sufficient proof of this.

Students are encouraged to pursue a course of study that shall form a sound foundation for their future technical work. They are encouraged to adopt applied

chemistry as a calling, but no appeal is made to them on the grounds that it is a profession.

The neglect of this cardinal fact has led to the present deplorable state of things.

It is the first duty of a chemical professional body to encourage the development of a professional spirit—which at present is almost entirely wanting—and to include in the profession all those who are actively and personally engaged in applied chemistry.

As your correspondent points out, there are many men, with perhaps slender academic qualifications, whose technical qualifications fully entitle them to speak with authority.

It may be added that there are an even larger number of younger men who have not had either time or opportunity to prepare for purely educational tests and whose technical experience is naturally inconsiderable.

To deny by implication that both these types of men have no professional status is an absurdity and worse than an absurdity.

A professional organisation is needed that has broad and sympathetic views and the will to follow and enforce a strong policy in order that the chemical profession may ultimately rank equally with other great professions, and that its members may, without distinction, obtain the status to which their services entitle them.—I am, &c.,

J. WILBERFORCE GREEN, Secretary,
The Association of Chemical Technologists.

30, Victoria Street, Westminster, S.W.,
Jan. 21, 1914.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 23, December 8, 1913.

Transformation of Essence of Citron into Essence of Roses.—Ph. Barbier and R. Locquin.—The authors have found that by the action of various reagents, such as the hydracids, for example, it is easy to transform citronellol into rhodinol, but the reverse change cannot be effected. This explains why commercial citronellols frequently smell of rhodinol, and also why, starting from either *d*-citronellol or *l*-rhodinol, various authors have obtained the same derivatives. Thus the three rhodinols foretold by theory are actually known, viz.:—(i.) The *l*-rhodinol of essence of roses or of pelargonium; (ii.) the *d*-rhodinol which is obtained by the transposition of *d*-citronellol or indirectly from natural *d*-citronellol; (iii.) the *i*-rhodinol prepared by MM. Bouveault and Gourmand by the reduction of synthetic ethyl rhodinate.

Neutralisation of Peroxidic Acid.—René Dubrisay.—By the method of capillary volumetry which he has previously described the author has proved that peroxidic acid is tribasic. In order to demonstrate the third basicity it is necessary to work with very dilute solutions, and it appears that the capillary method is more sensitive than the method of electric conductivity for the study of neutralisation. The third basicity of both phosphoric and peroxidic acids is detected thus, while conductivity determinations do not reveal it.

Action of Carbon Oxychloride on Phosphates and Silicates.—J. Barlot and Ed. Chauvenet.—When phosphates are exposed to the action of COCl_2 at temperatures of from 350° upwards the following reaction occurs: $\text{P}_2\text{O}_5 \cdot 3\text{MO} + 6\text{COCl}_2 = 2\text{POCl}_3 + 6\text{CO}_2 + 3\text{MCl}_2$. With silicates the reaction is $\text{SiO}_2\text{M} + \text{COCl}_2 = \text{SiO}_2 + \text{CO}_2 + \text{MCl}_2$. Thus phosgene gas is a very suitable reagent for attacking phosphates and silicates in order to analyse them, or for

preparing anhydrous metallic chlorides from these minerals. Whatever the state of combination of the metal (oxide, sulphide, nitrate, carbonate, sulphate), it is readily transformed into anhydrous chloride.

Nitration of Paraiodoacetanilide.—E. Jungfleisch.—By varying the experimental conditions the nitration of paraiodoacetanilide can be made to yield either the isomer $\text{C}_6\text{H}_4\text{I}(\text{NH}_2)^1$, or a mixture of products including the acetyl derivative of *para*-nitroaniline, diiodo-acetanilide, the acetyl derivative $\text{C}_6\text{H}_3\text{I}_2(\text{NO}_2)(\text{NHCOCH}_3)^1$, and a substance which appears to be the acetyl derivative of an iodonitraniline.

Bulletin de la Société Chimique de France,
Vol. xiii.-xiv., No. 20—21, 1913.

New Preparation of Epichlorhydrine.—Jean Nivière.—Epichlorhydrine can be prepared by the action of quicklime on symmetrical dichlorhydrine. The lime is placed in a flask which is heated on a water-bath, the pressure being reduced to 120 mm. The dichlorhydrine is allowed to fall in drop by drop, and epichlorhydrine then distils over. The yields are very satisfactory, 93 to 95 per cent of the theoretical amount of pure epichlorhydrine being obtained, boiling at $116-119^\circ$, after drying over K_2CO_3 .

Action of Dimethylamine upon the Iodohydrines Derived from Styrolene. Study of the Two Phenyl-dimethylamino-ethanols. — M. Tiffeneau and E. Fournieu.—The authors have prepared two isomeric iodohydrines from styrolene; the one, $\text{C}_6\text{H}_5\text{CHOH}\cdot\text{CH}_2\text{I}$, is obtained by the action of iodine and mercuric oxide on styrolene in solution in aqueous ether, while the other, $\text{C}_6\text{H}_5\text{CHI}\cdot\text{CH}_2\text{OH}$, which is crystalline, is formed by the fixation of HI on styrolene oxide. When these two compounds react with dimethylamine in the cold they yield the same amino-alcohol. This amino-alcohol is different from that which would normally be obtained with the crystallised iodohydrine, if the intermediate formation of oxide of styrolene, $\text{C}_6\text{H}_5\text{CHN}(\text{CH}_3)_2\cdot\text{CH}_2\text{OH}$, did not occur. This amino-alcohol can be prepared from the corresponding etherified acid, $\text{C}_6\text{H}_5\text{CHN}(\text{CH}_3)_2\cdot\text{CO}_2\text{C}_2\text{H}_5$, by reduction by Blanc and Bouveault's method. This latter amino-alcohol is quite different from that furnished by the iodohydrines. Thus it has been proved, as far as the halogen hydrines are concerned, that the intermediate formation of oxide of ethylene occurs, so that ammonia and the primary and secondary amines cannot be used to determine the structure of the halogen hydrines. The authors have prepared many derivative of the two amino-alcohols.

Constitution of Trinitro-*p*-aminophenols and of Trinitro-*p*-anisidines.—Frédéric Reverdin and Raphael Meldola.—Two isomeric trinitro-*p*-anisidines are known of m. p. $127-128^\circ$ and $138-139^\circ$ respectively. One of their nitro-groups is extremely mobile, and many syntheses have been effected owing to this property. The authors have arrived at the general conclusion that in the latter it is always the nitro-group at 3 which is mobile, while in the isomer of melting-point 127° it is the group at 2 which is mobile under the influence of basic reagents, while the 3-group is mobile after diazotation under the influence of the neighbouring diazo-group. They have also proved that the original trinitroacetylaminophenol, from which the anisidines were derived, was not the 2.3.5- but the 2.3.6-compound.

Soluble Caseins in Milk.—L. Lindet.—The author has confirmed his previous results relating to the presence of two soluble albuminoids in milk, and has further shown that the sum of these two caseins is practically constant, although the proportion of each of them is very variable. They adhere by capillarity to the casein in suspension.

Determination of very Small Quantities of Chlorides in Waters.—Maurice Lombard.—150–200 cc. of water are boiled until all the calcium bicarbonate is decomposed; the water is allowed to cool, it is brought up to its original

volume, and 100 cc. of the clear liquid are poured off. Then 5 drops of a 10 per cent solution of potassium chromate are added, and the same quantity to 100 cc. of distilled water containing, say, 5 mgrms. of NaCl per litre. Standard silver nitrate solution is then added to the known solution till a sufficiently distinct coloration is obtained, and then the silver nitrate is added to the water under examination until precisely the same tint is obtained. The calculation is very simple. If, for example, 1.8 cc. was added to the known solution (100 cc. of NaCl containing 5 mgrms. per litre) and 2.65 to the unknown solution, then $2.65 \div 1.8$ or 0.85 cc. correspond to 0.497 mgrm. of NaCl, which added to the 0.5 mgrm. in the comparison solution gives 1 mgrm. of sodium chloride in 100 cc., or 10 mgrms. per litre. The method is very sensitive, and quantities of chloride which are less than 0.5 mgrm. per litre can be determined by it.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvii, No. 14, 1913.

Organic Silicon Compounds from Silicon Hexachloride and Methyl Magnesium Bromide or Iodide.—Geoffrey Martin.—The author has already described the formation of a substance, approximately of the composition $\text{CH}_3\text{Si}_6\text{O}_{13}\text{H}_9$, which, when dissolved in caustic potash, liberates about 169 cc. of hydrogen per gram. By varying the experimental conditions compounds containing more methyl groups can be obtained, e.g., $(\text{CH}_3)_2\text{Si}_6\text{O}_{12}\text{H}_6$, $(\text{CH}_3)_4\text{Si}_6\text{O}_{12}\text{H}_2$, $(\text{CH}_3)_5\text{Si}_6\text{O}_{11}\text{H}$, and $(\text{CH}_3)_8\text{Si}_6\text{O}_7\text{H}_2$. The quantity of hydrogen generated is less the greater the number of methyl groups present in the molecule. In the course of these experiments the author has prepared Bygden's hexamethyl-silicoethane, $\text{Si}_2(\text{CH}_3)_6$, and investigated its chemical properties. This substance does not liberate hydrogen on treatment with caustic potash, although it contains the Si—Si group.

Manganese Carbides and their Preparation by Heating the Metal in a Current of Methane.—Siegfried Hilpert and J. Paunesco.—When finely powdered manganese is treated with methane or methane and hydrogen at temperatures from 600–900° carbides result. With pure methane carbides containing up to 20 per cent C can be obtained, and with mixtures of equal volumes of methane and hydrogen carbides containing 15 per cent C. The saturation limits established for different temperatures do not correspond to simple atomic proportions. From their behaviour towards acids it may be deduced that the carbides are not derivatives of simple hydrocarbons, like calcium and aluminium carbides. Carbides containing up to 7 per cent C are ferromagnetic.

Modifications of Phosphorus.—Alfred Stock and Erich Stamm.—Smits and Leeuw have stated that different modifications of phosphorus exist in the melt of colourless phosphorus, and that the ordinary melting-point of colourless phosphorus (44.1°) is raised several degrees if the substance is first heated to 100° and then rapidly cooled. The authors cannot confirm these results. From the study of the melting- and solidification-points of red phosphorus it is observed that the melts behave like solutions and not like simple substances. The vapour arising from red phosphorus consists chiefly of P_4 . From superheated phosphorus vapour more red phosphorus is deposited than was dissociated, so that obviously P_4 molecules take part in the formation of molecules of red phosphorus.

MISCELLANEOUS.

Royal Institution.—On Thursday next, February 5, at 3 o'clock, Prof. Sir Thomas H. Holland begins a course of two lectures on "Types and Causes of Earth Crust Folds." The Friday Evening Discourse on February 6 will be delivered by Dr. H. S. Hele-Shaw on "The Mechanics of Muscular Effort"; and on February 13, by

Prof. J. Norman Collie, on "Production of Neon and Helium by Electric Discharge."

Economical and Accurate Testing of Mixtures without Weighing.—Manufacturers are often impressed with the time occupied in weighing the different ingredients required in the constitution of their several articles of manufacture; and, what is of still more importance, the accuracy of the several weighings are liable to serious irregularities. These several obvious requirements have induced Messrs. W. and T. Avery, Ltd., of the Soho Foundry, Birmingham, to design and manufacture a machine which exactly meets the case. The machine is of simple yet solid design. The steelyard is graduated to meet the wishes of the manufacturer, and buckets are hung from each of the hooks. In this case a quantity of one ingredient is placed in the bucket on the left of the fulcrum, and the moving poise is placed on the 20 per cent graduation, and when the latter balances the steelyard the ingredients will be found to be in the proportion of 80 and 20. The steelyard can be marked in any desired manner to suit the requirements of any particular trade, effecting a great saving in time and ensuring absolute accuracy. This machine can also be arranged to weigh the total of the mixture.

MEETINGS FOR THE WEEK.

- MONDAY, Feb. 2nd.**—Royal Institution, 5. General Meeting. Society of Chemical Industry, 8. "Oxygen and Metallic Antimony in Crude Antimony," by W. R. Schoeller. "Estimation of Zinc in Coinage Bronzes by Volatilisation," by T. K. Rose. "Nickel Tannates," by P. Singh. Opportunity will be given for discussing the following Paper:—"The Electrical Conductivity of Milk during its Concentration, with suggestions for a Practical Method of Determining the End-point in the Manufacture of Sweetened Condensed Milk," by L. C. Jackson, L. McNab, and A. C. H. Rothera.
- Royal Society of Arts, 8. (Cantor Lecture). "The Relation of Industry to Art," by Sir Charles Waldstein, Litt.D., Ph.D.
- TUESDAY, 3rd.**—Royal Institution, 3. "Animals and Plants under Domestication," by Prof. W. Bateson, F.R.S., &c. Royal Society of Arts, 4.30. "The Montreal, Ottawa, and Georgian Bay Canal," by Sir Robert Perks, Bart.
- WEDNESDAY 4th.**—Society of Public Analysts, 8. (Annual General Meeting). "Iodometry of Arsenic, Copper, and Iron," by G. D. Lander and J. J. Geake. "Composition and Analysis of Compound Liqueur Powder," by A. E. Parkes and F. Major. "Composition of the Saline Matter adhering to certain Wet Salted Skins," by M. C. Lamb.
- Royal Society of Arts, 8. "Motor Fuels, with special reference to Alcohol," by William Ormandy, D.Sc., &c.
- THURSDAY, 5th.**—Royal Institution, 3. "Types and Causes of Earth Crust Folds," by Prof. Sir T. H. Holland, F.R.S. Royal Society. "Conduction of the Pulse Wave and the Measurement of Arterial Pressure," by L. Hill, J. McQueen, and M. Flack. "Report of the Monte Rosa Expedition of 1911," by J. Barcroft, M. Camis, C. G. Mathison, F. Roberts, and J. H. Ryffel. "Notes on Soil Protozoa," by C. H. Martin and K. Lewin. "Development of the Starfish *Asterias Rubens*, L.," by J. F. Gemmill. "Floral Mechanism of *Weiwitschia Mirabilis* (Hook)," by A. H. Church.
- Chemical, 8.30. "Absorption Spectra of the Vapours and Solutions of various Substances containing Two Benzene Nuclei," by J. E. Purvis. "Oxidation of some Benzyl Compounds of Sulphur—Part II., Benzyltetrasulphoxide," by J. A. Smythe. "Reaction between Iodine and Aliphatic Aldehydes," by H. M. Dawson and J. Marshall. "Erosion of Lead," by J. F. Liverseege and A. W. Knapp. "Acylation as Influenced by Steric Hindrance—The Action of Acid Anhydrides upon 3,5-Dinitro-*p*-aminophenol," by R. Meldola and W. F. Holley.
- FRIDAY, 6th.**—Royal Institution, 3. "The Mechanics of Muscular Effort," by H. S. Hele Shaw, F.R.S.
- SATURDAY, 7th.**—Royal Institution, 3. "Neglected Musical Composers," by Prof. F. Corder.

THE CHEMICAL NEWS.

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HISTORY OF THE DISCOVERY OF FORMIC ACID.

By F. D. CHATTAWAY.

BEFORE the beginning of the sixteenth century some naturalist had observed with surprise that the blue flowers of chicory became reddened when thrown upon an ant-hill. This fact is recorded by early writers on botany—thus Brunfels* in 1536 writing of chicory, which he calls "Solsequium," "Cicnoriun," or "Sponsa sois," says:—"Flos eius iniectus formicarum cumulo in rubrum vertitur colorem, idque in magno naturae miraculo," and Hieronymus Tragus† a little later, in 1552, makes a similar but more elaborate statement:—"Scu quod fere preterieram, nature miracula in hoc quoque flore observare licet. Siquidem non tantum ad sois ortum et occasum sese pandit et recludit utrum etiam cumulo formicarum abditus caeruleum colorem in rubeum mutat, ac si terrore illarum erubesceret."

The observation evidently aroused interest, for it is quoted by later writers. Thus Langham,‡ in the "Garden of Health," writes in 1577:—"Cast the flowers of Cycory among a heap of Ants or Pismires and they will soon become as red as blood"; while Bauhinus,§ more than half a century later, repeats the statement of Brunfels:—"Flos Solsequi ut Brunfels annotat seu Cicnori, iniectus formicarum cumulo in rubrum vertitur colorem, idque in magno naturae miraculo."

Our exact knowledge of formic acid, however, really begins with a letter of John Wray|| published in the *Transactions of the Royal Society*¶ for 1670, in which he compares the statements of two friends, Dr. Hulse and Mr. Samuel Fisher, an account of an acid liquor obtained by distilling ants with water. Wray was apparently only interested in the matter as a curious phenomenon, and wrote the letter with a view to elicit further investigation. As was his wont he fully acknowledged the sources of his information, and says that what he sends "concerning the Juyce of Pismires" he received from Dr. Hulse and Mr. Samuel Fisher,** of Sheffield. The former having

met with the passage quoted above from Langham had written to Wray, as follows, in a letter dated Aug. 10th, 1669:—"I presently got some Chicory flowers and made the Experiment, and find it to be true what he saith, only he takes no notice of the manner how the flowers come to be stained; which therefore take as follows: Bore an Ant-hill with a stick, and then cast the flowers upon it and you shall see the Ants creep very thick over them. Now as they creep they let fall a drop of liquor from them and where that chanceth to light there you shall have in a moment a large red stain. Sometimes they will be a pretty while before they discolour them and at other times they will do it suddenly. At first I guessed that being vexed by stirring their hill they might thrust their stings into the flowers, and thorow them convey that sharp liquor. But by bruising them and rubbing the expressed juyce against the flowers I find they will be equally stained. 'Tis a thing well known that Ants, if they get into people's clothes and so to their skin, will cause a smart and tingling as if they were nettled; which I conceive is done by letting fall the fore-mentioned corrosive liquid rather than by stinging. To what sort of liquor to refer this Juyce I know not. . . ."

On reading this letter Wray called to mind an experiment which Mr. Samuel Fisher, of Sheffield, had made him acquainted with some years before, that "If with a staff or other instrument you stir an heap of Ants (especially Horse-Ants) so as to anger them they will let fall thereon a liquor which, if you presently smell to, will twinge the Nose like newly distilled Spirit of vitriol." He thereupon sent to enquire of Mr. Fisher what "Trials he had made of it," and received in reply the following account:—

"A weak Spirit of Pismires will turn Borage flowers red in an instant. Vinegar a little heated will do the like. Pismires distilled by themselves or with water yield a Spirit like Spirit of Vinegar, or rather like the Spirit of *Viride aeris*. Lead put into this Spirit, or fair water, with the animals themselves being alive, maketh a good Saccharum Saturni . . . when you put the Animals into water you must stir them to make them angry and then they will spirt out their acid juyce."

Fisher continues that he is not acquainted with any other animal that on distillation yields an acid spuit, and asks "whether any ingenious person conversant in these inquiries hath either himself found out or heard of any other animal that by distillation or otherwise yields an acid spuit."

Wray states that he has not, and adds*:—"Indeed, it seems strange that nature should prepare and separate in the Body of this Insect without any sensible heat and that in good quantity considering the bulk of the animal, a liquor the same for kind with those Acid Spirits which are by Art extracted out of some minerals not without great force of Fire." He concludes:—"I doubt not but this liquor may be of singular use in medicine. Mr. Fisher hath assured me that he himself hath made trial thereof in some diseases with very good success."

The acid liquid obtained from ants naturally attracted from time to time the attention of chemists, who at first concerned themselves with demonstrating the individuality of the acid and preparing its various salts. No considerable additions to the observations of Hulse and Fisher were, however, made till Margraf, about the middle of the eighteenth century, took up the study of the acid.

He writes†:—"During the months of May and June of this year (1749) I collected a quantity of these lively little

* Brunfels Otto (Brunfelsius Otho, "Herbarum vivae eicones . . . Argentorati apud Joannem Schottu, 1530-1531-1536," vol. iii., published 1536, p. 95). Mrs. Arber, to whose kindness I am indebted for these references, writes:—"Since Brunfels derives nearly all his text from previous writers, especially Dioscorides, I should expect that the statement about the ants and chicory did not originate with him. He says himself that his descriptions are 'extracted from ancient and trustworthy authors.'"

† Hieronymi Tragi, de stirpium, maxime earum, quae in Germania nostra nascuntur," Lib. I., Cap. xcii., page 271. (Argent, 1552, 4°).

‡ "The Garden of Health"; Conteyning the sundry rare and hidden virtues and properties of all kinds of simples and plants, together with the manner how they are to be used and applied in medicine for the health of man's body, against divers diseases and infirmities common amongst man. Gathered by the long experience and industry of William Langham, Practitioner in Physicke. Imprinted at London, 1577. Page 144 at end of section on "Cicory."

§ Bauhinus, "Historiae plantarum universalis," Tom II., Lib. xxiv., page 1010. (Lobduni, 1651).

|| John Wray (1627-1705), the distinguished naturalist and botanist. In his letter to the Royal Society he spells his name Wray, but later in the same year dropped the initial W. He refers to the change in a letter to Dr. Listr., dated Aug. 22nd, 1670, where he tells him that he resumes the name of Kay, Wray being contrary to the way of his forefathers writing their names. He was, however, apparently also influenced by the circumstance that it was not possible to Latinise Wray. He used Wray all the time he was at Cambridge, his name being always thus spelt in the registers of Trinity College.

¶ *Phil. Trans.*, 1670, v., 2063. Extract of a letter written by Mr. John Wray to the publisher, dated Jan. 13, 1670, "Concerning some uncommon Observations and Experiments made with an acid Juyce to be found in Ants."

** Kopp, *Geschichte der Chemie*, iv., 362, refers incorrectly to Wray's Sheffield friend as "Samuel Fischer—a German," but states that he has not been able to get exact information on the point.

* It may here be noted that comparatively strong formic acid is ejected as a means of defence by various caterpillars. Wilt (*Jan. suerente*, 1847-1848, p. 546) has shown that in caterpillars and especially in the Processions caterpillar (*B. mor. proc.* on *a*) formic acid is present in the tree concentrated condition, and Poulton (*B. u. Ann. R. p.*, 1887, p. 765) has described how the larvae of the genus *Cerura* (*D. annura*) have the power for purposes of defence of ejecting, when disturbed, a secretion containing about 40 per cent of formic acid. A larva which has not been irritated previously will eject 0.05 grm. of such a liquid.

† "Opusculum Chymiques," Paris, 1762, vol. i., page 294.

animals intending to extract not only the oil which they contain but also the acid. To this end I put them into an ample glass retort, poured in water, and placed it in a capsule of sand. Having adapted a suitable receiver and luted the joints I undertook the distillation, gradually increasing the heat until the water boiled. . . . I found in the receiver a water which was somewhat acid with the essential oil of ants floating on the surface. I separated this oil from the water as one ordinarily does it with some cotton, and preserved it in spirit."

The acid liquid he re-distilled and combined the distillate with the alkaline earths and the alkalis.* From an examination of the salts produced, Margraf concluded that the acid, while resembling in many respects the acid of vinegar, did not possess all the properties of the latter. The study of the acid was continued in a careful and systematic manner by Arvidson and Oehrn,† who described it and its salts with great exactitude. They supported Margraf's view that formic acid was not identical with the acid of vinegar by showing that if solutions of the two acids of the same specific gravity were prepared a given quantity of any base did not require the same amount of each for neutralisation. Deyeux‡ also about the same time expressed the opinion that formic acid was "un acide *sui generis*" though closely resembling acetic acid in properties.

Hermstadt§ some few years later occupied himself specially with the purification of the acid, but came to the erroneous conclusion that malic acid was present in the expressed juice of ants.

Richter,|| in 1793, showed how the acid might be concentrated by combining it with potash and distilling the dry salt with the exact amount of sulphuric acid, diluted with its own weight of water, required to neutralise the base used.

Some few years later, Fourcroy and Vauquelin advanced the statement, based on very superficial and insufficient work, that the acid obtained from ants was in reality a mixture of acetic and malic acids.¶

The contradictory statements which had been made up to this time respecting the acid induced Suersen** to submit it again to examination. In a dissertation published in 1805 he showed that the experiments of Fourcroy and Vauquelin did not justify their conclusions. He proved that formic acid suitably purified did not contain malic acid, and that it differed from acetic acid in several of its properties.

In 1812 Gehlen†† having prepared with great care formic and acetic acids and the copper and barium formates and acetates, compared their properties anew. He both criticised previous work, and pointed out with great clearness the peculiar characters of formic acid, and thus definitely established its individuality.

Berzelius‡‡ attempted in 1817, but with no great success, to determine the percentage composition of formic acid. This was first done in 1834 by Liebig, who employed his new method of elementary analysis.

In his famous essay upon manganese Scheele§§ records,

* Thouvenal (1747-1815) used an ingenious method to obtain formates. He spread linen impregnated with potash on uncovered ant-hills, "the ants running over the cloth emitted their acids and odorant principle of the same nature which they exhaled in so great an abundance as to saturate the fixed alkali spread on the cloth. The lixivium of these linens afforded by evaporation a neutral salt crystallised in flat parallelograms and prismatic columns which were not deliquescent." Fourcroy's "Chemistry," London, 1788, vol. iv., p. 422.

† "Dissertatio chemica de acido formicarum," Upsala, 1777.

‡ *Journal de Physique*, 1778, xxii., 352.

§ "Physikalisch-chemische Versuche und Beobachtungen, 1789, vol. ii., pages 5-36.

|| *Ueber die neuern Gegenstände der Chemie*, 1796, vi., 135.

¶ *Annales du Muséum National d'Histoire Naturelle*, vol. i., page 333; Gehlen's *Journal der Chemie*, 1804, ii., 42. They afterwards admitted that they had mistaken phosphoric acid, which the juice of ants contains, for malic acid.

** Gehlen's *Journal der Chemie* 1805, iv., 3.

†† Schweigger's *Journal. Chem. u. Phys.*, 1812, iv., 1-41.

‡ *Annals of Philosophy*, ix., 107; *Ann. Chem. Phys.*, iv., 109.

§§ *K. Svenska Vet. Akad. Handl.*, 1774, xxxv; "The Chemical Essays of William Scheele," Beddoes Translation. London, 1786, p. 97.

in 1774, that when diluted vitriolic acid sugar and manganese are heated together "there arises a vapour that vellicates the nose, and if it be collected in a receiver appears to be pure vinegar." Westrumb later, in 1785, mentions that vinegar is produced by the dephlogistication of tartaric acid by means of oxide of manganese.

Dobereiner, in 1822, showed that the acid produced in this reaction is really formic acid. He says*:—"If tartar or tartaric acid and black oxide of manganese are placed in water and the mixture warmed, violent action ensues. The temperature rises, and a large quantity of carbonic acid gas is evolved. There distils over at the same time a clear liquid which superficially resembles acetic acid, but is shewn by a more exact examination to be formic acid." He discovered that the acid had the property of reducing the salts of the noble metals, and that it breaks up into water and carbonic oxide under the influence of sulphuric acid.

Dobereiner described later a method of preparing formic acid artificially in large quantity by the oxidation of sugar. He writes†:—"Should chemists and physicians make use of formic acid and its compounds they can be most advantageously obtained according to my experience by the partial oxidation of sugar," and then describes the process.

"A solution of 1 part of sugar in 2 parts of water is heated to 60° C. with 2½ or 3 parts of finely powdered manganese dioxide in a copper still, which, as the liquid is very apt to froth up, must have at least fifteen times the bulk of the mixture; a third part of a mixture of 3 parts oil of vitriol, and 3 parts water is then gradually added, whereupon carbonic acid gas loaded with vapour of formic acid immediately escapes with violence. The head and condensing tube must now be quickly put on, and when the violent action has subsided the other two-thirds of the dilute sulphuric acid added, the mixture being stirred all the while, after which the liquid is gradually distilled almost to dryness. The distillate, which is transparent and colourless, is saturated with chalk, and the filtrate evaporated to the crystallising point, or if it be desired to obtain the acid the distillate is saturated with sodium carbonate, evaporated, and 7 parts of the dry residue distilled with a mixture of 70 parts oil of vitriol and 4 parts of water.

"This process is a very good one, 1 pound of sugar gives as much formic acid as will saturate 5 to 6 ounces of calcium carbonate, but the formic acid which it yields is slightly contaminated with acetic acid. To remove this impurity the distillate should be saturated while yet warm, not with sodium carbonate, but with carbonate of lead, and the solution evaporated to the crystallising point; the more soluble acetate of lead remains principally in the mother-liquor, and the formate of lead thus obtained must be distilled with a mixture of equal parts of oil of vitriol and water."

Wohler, later,‡ found it advantageous to use starch, and Liebig§ gives a method which differs little from Dobereiner's, except that starch is used in place of sugar.

In 1831, Pelouze|| discovered that formic acid could be obtained from hydrocyanic acid and the cyanides. Anhydrous hydrocyanic acid was mixed with about its own volume of fuming hydrochloric acid. After four to five minutes the liquid solidified to a crystalline mass with sensible disengagement of heat. This was submitted to distillation, when it volatilised without residue, and gave successively hydrocyanic acid, hydrochloric acid, formic acid, and finally ammonium chloride. Pelouze also found that when a concentrated aqueous solution of potassium cyanide was boiled, out of contact with air, ammonia was liberated, and potassium formate produced. The hydrolysis of the cyanide at first took place rapidly, but as the action proceeded became slower and slower, and was not com-

* Gilbert's *Annalen*, 1822, lxxi., 107.

† *Annalen*, 1832, iii., 141.

‡ *Pogg Ann.*, 1829, xv., 307.

§ *Annalen*, 1836, xvii., 69.

|| *Ann. Chem. Phys.*, 1831, xlviii., 395.

plete even after the evaporated water had been several times renewed. He also showed that ammonium formate decomposed at about 180° into hydrocyanic acid and water. Only traces of formate escaped decomposition when the distillation was carried out in a narrow tube plunged in a long column of mercury heated to 180–200°. The product of the distillation was very concentrated hydrocyanic acid.

Geiger* appears to have observed, independently of Pelouze, that when an aqueous solution of potassium cyanide is evaporated, potassium formate is contained in the residue.

The relationship of formic acid to methyl alcohol was established† in 1835 by Dumas and Peligot. These chemists found that although wood spirit could be left in contact with air without change, e.g., in a badly stoppered bottle, if the vapour mixed with air was brought into contact with finely divided platinum, heat was evolved and formic acid produced, just as acetic acid was produced under the same conditions from ordinary alcohol.

THE PHENOMENA OF PASSIVITY.‡

By MAX LE BLANC (Leipzig).

IN response to the kind invitation of the Faraday Society, I take the opportunity of giving a brief survey of the phenomena of passivity, and I shall attempt to present them viewed from a uniform standpoint.

The first observations relating thereto are more remote than one usually supposes; even at the end of the eighteenth century, at the time of the discovery of galvanism, James Keir (*Phil. Trans.*, 1790, lxxx., 374), following on still earlier experiments by Bergmann, remarked that when he poured an unsaturated solution of silver in pure colourless nitric acid upon a piece of pure iron wire, a reaction did indeed take place at first, with the separation of metallic silver; but the action of the iron upon the liquid soon ceased and the silver re-dissolved. Then for several weeks the iron lay at the bottom of the vessel, apparently unchanged and bright.

It is interesting to note that Keir became aware of the instability of this peculiar condition; it was lost by scratching the piece of iron, as also by touching it with a new piece.

The phenomenon was not then further investigated until 1827, when it was re-discovered by Wetzlar (*Schweigger's Journ. f. Chemie u. Physik*, 1827, xlix., 470; 1., 88, 129), who drew attention to electrochemical relations. Fechner (*Ibid.*, 1828, liii., 141) then made electrical measurements, which showed that by forming an element of iron-silver in a silver solution the iron remained electropositive so long as it possessed the power of dissolving spontaneously and reacting chemically. As soon as this power disappeared it became electronegative.

At the end of the thirties the investigation was continued by Schönbein (*Pogg. Ann.*, 1836, xxxvii., 390, 590), who published a mass of new details; especially he showed that the inactive condition of iron can be brought about by making it in a suitable manner the anode in aqueous, even dilute solutions of different oxyacids. He introduced the expression "passive," which has ever since been retained.

At this time it was known that other metals than iron could also assume this peculiar property of passivity.

Attempts to account for the phenomena of passivity have naturally been made. The discoverer himself, Keir, had thought about the matter, as can be seen from the closing words of his paper:—"The explanation of these phenomena will be attempted in the subsequent paper." This promise, however, he did not fulfil.

Fechner thought of the formation of a protective coat, but inspection by another person convinced him that the iron was so bright that, to him, oxidation seemed quite out of the question.

Faraday (*Phil. Mag.*, 1836, ix., 61) held a different opinion, and expressed himself thus:—"My strong impression is that the surface of the iron is oxidised, or that the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation; and that having thus their affinity for oxygen satisfied, and not being dissolved by the acid under the circumstances, there is no renewal of the metallic surface, no reiteration of the attraction of successive particles of the iron on the elements of successive portions of the electrolyte, and therefore not those successive chemical actions by which the electric current (which is definite in its production as well as in its action) can be continued."

This oxide theory, with numerous modifications, has been adopted up to quite recent times by a large number of investigators without any surer proof of its correctness having been brought. On the other hand, certain facts have become known which either cannot or only with difficulty can be brought into line with the theory of an oxide layer forming a protection for the electrode. Most important is the discovery of Müller and Königsberger (*Zeit. Elektrochem.*, 1907, xiii., 659; 1909, xv., 742), according to whom the reflecting power of iron in alkaline solutions is identical in the active and in the passive state; they proved, however, that a layer of lead peroxide of approximately molecular thickness (0.8 μ) deposited upon a platinum mirror greatly diminished the reflecting power of the mirror, and the optical constants of the known iron oxides and hydroxides differ only very slightly from those of lead peroxide; hence these workers both come to the conclusion that the passivity of iron is not occasioned by a coating of oxide.

Krüger ("Vortrag auf der Hauptverslg. der Deutschen Bunsen Ges. zu Breslau," 1913) has recently come to the same conclusion by measuring the reflecting powers of passive and active iron for ultra-red rays.

One may object that the hypothetical oxide may have other properties than the known oxides, but one would have to confess that such an *ad hoc* supposition would be arbitrary and improbable. The same can be said of the supposition that the layer is so extremely thin that it only just covers the surface, but cannot be detected by even the most sensitive optical method. It is indeed not comprehensible on what grounds the protective layer should be formed in just such small dimensions, for in those cases in which no one doubts the formation of oxide—as, for example, in the case of the anode treatment of lead electrodes in sulphuric acid or in sodium chromate solution—the conducting metallic oxide which covers the surface after a short time becomes easily visible to the naked eye.

Such firmly adherent anodic layers, which protect the underlying metal, are always accompanied in electrolysis by simultaneous evolution of oxygen if the electrolyte consists simply of a salt, whose anions form with the anode metal a difficultly soluble compound (Le Blanc and Bindshedler, Isenburg Just, *Zeit. Elektrochem.*, 1902, viii., 255; 1903, ix., 275, 577. Should, however, excess of another salt be added, whose anions form an easily soluble salt with the anode metal—e.g., sodium chlorate in the case of lead anodes in sodium chromate solution—there is neither evolution of oxygen nor the deposition of any firmly adhering precipitate on the anode, but a precipitate is quantitatively produced, which falls away from the electrode, which remains bare. This process has been applied for the technical production of difficultly soluble substances, such as white-lead, and it is based upon the fact that in consequence of the simultaneous action of the excess of chlorate ions nearest the electrode a layer of liquid free from chromate ions forms soon after the commencement of the electrolysis. This layer prevents the

* *Annalen*, 1832, i., 44.

† *Annalen*, 1835, xv., 1.

‡ Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, November 12, 1913.

formation of precipitate in the immediate vicinity of the electrode, and consequently also prevents any adhesion thereto.

How do *passive* electrodes behave in such cases? Nickel is passive under anodic treatment in pure potassium sulphate solution and oxygen is evolved; in pure sodium chloride solution it easily dissolves. On adding sodium chloride to the potassium sulphate solution, solution of the nickel still takes place with a moderate current density, whilst the evolution of oxygen ceases, but no detachable precipitate becomes visible. So that this observation is also unfavourable to the supposition that all cases of passivity are due to the formation of a good conducting protective layer on the electrode.

Furthermore, the strong influence of rise in temperature in restoring the activity of the metal concords ill with the oxide theory, whilst the remarkable instability of this layer must excite wonder, since it finds expression in the spontaneous return of the metal to a more or less active state when the means of bringing about the passive condition are withdrawn.

This last point has already been raised by Schönbein (*loc. cit.*) as an argument against the oxide theory of Faraday. The particular passage reads thus:—"A further and more important circumstance, to which attention must be drawn, is the fact that the iron wire, which dips in the dilute acid and remains indifferent to it, becomes attacked as soon as the electric current no longer passes through it. For instance, by leaving the wire dipping in the acid and opening the circuit in some way, there appear instantly yellowish brown streaks shooting downwards, *i.e.*, ferric nitrate. . . . It is also clear that if the passivity of the positive iron wire be due to a film of oxide upon it, then the same wire, when removed from the circuit and placed in ordinary nitric acid, should remain passive; but this is not the case."

Thus from the various facts quoted, which can also be amplified, it is evident that the hypothesis of an impervious layer, which covers the surface of the metal, thereby protecting it from contact with the electrolyte, is open to the most serious objection.

We shall therefore attempt to arrive at an understanding of the phenomena of passivity on other grounds; this brings me to the polarisation measurements for metals, immersed in their respective salt solutions, which I carried out some years ago (*Le Blanc, Abhandlungen d. Deutschen Bunsen Ges.*, 1910, No. 3). Although these measurements may seem to have little to do with the problem in hand, we shall presently see that they can be brought to bear very closely upon it.

Let us take as our basis for the calculation of the potential difference at a metallic electrode Nernst's formula—

$$E = \frac{RT}{n_e F} \log \frac{P}{p}$$

(R = gas constant; T = abs. temp.; n_e = valency of the metal; F = 96,540 coulombs; P = constant for a given metal under given conditions (the electrolytic solution pressure); p = osmotic pressure of the corresponding metal ions). Let us suppose also that the formula can be applied for any desired variable condition, so long as it be reversible; then at constant temperature polarisation, and consequently a rise in potential difference, can only occur in consequence of a change in value of P or of p . If we exclude the former by using a specified metal electrode, the electrode potential can only be changed by changing p , or, since p depends upon the concentration of the solution of metallic salt, simply by changing the concentration of the solution.

From this point of view we might expect that when employing a system: metal—a not too dilute solution of a metallic salt—metal (*e.g.*, copper-copper sulphate solution-copper), no appreciable polarisation would take place in the case of a short-timed electrolysis with a moderate current density, for under such circumstances no marked

change of concentration of the electrolyte at the electrodes can occur. This expectation was fulfilled in the cases of the systems: lead-lead nitrate solution-lead; and mercury-mercurous nitrate solution-mercury; in all the other cases that were tried, anodic, and at the same time cathodic, polarisation occurred in spite of an ample ion concentration; especially was this the case in the systems: copper cupric sulphate or chloride in water-copper; silver-silver nitrate solution in water or in acetonitrile silver; iron-ferrous chloride in water-iron; nickel-nickel chloride in water-nickel. The degree of polarisation was dependent on many influences; for example, on the current density, the temperature (with rise of which it decreased), and the condition of the electrodes and solution. In many cases it could be greatly increased by addition of extremely small quantities of strychnine, brucine, gelatin, &c., and, indeed, always both at the anode and the cathode; the increase amounted to several tenths of a volt.

How can these facts be explained? Let us disregard the unlikely supposition that alternating obstructions oppose the processes of charging and discharging. Is there, however, not the possibility that the interchange of charge may be associated with a chemical reaction of changing velocity?

If we first consider the action at the anode, it is conceivable that primarily no metal ions are formed, as generally supposed, but that the electrical process consists of a discharge of negative ions and the chemical process of an interaction between the non-electrified radical and the metal. The potential difference would, according to this view, depend upon not only the concentration of the negative ions, but upon that of the separated non-electrified radical, and consequently upon the velocity with which the latter reacts upon the metal. For the smaller this is (*ceteris paribus*), the greater must the concentration become for a given current density, until the velocity of the reaction, which by the law of mass-action also increases, has become so great that in unit time as much of the radical disappears through chemical action as is produced by the electric current.

This view is certainly justified for series of solids, such as silver-silver sulphate or chloride-silver, which according to the researches of Haber and Zawadzki (*Zeit. Phys. Chem.*, 1911, lxxviii., 228) even at low temperatures show considerable polarisation at the anode; nor can any serious objection be made to its application to the series of liquids quoted above, but in the latter case we are not obliged to relinquish the usual idea of the preliminary formation of metallic ions, in order to be able to assign the observed polarisation to failing chemical reaction velocity; we need only adduce the probable extensive hydration of the metal ions (or their combination with the solvent). The process of hydration which occurs at the surface of the electrode, and whose velocity depends on different influences, must, as shown in the introduction, then follow on the formation of ions, which, when the current passes, is practically infinitely rapid. The magnitude of the potential difference is then, it should be carefully remarked, dependent only upon the concentration of the non-hydrated, free ions, and the latter again upon the velocity of hydration. In this way polarisation, which changes according to circumstances, easily explains itself—also its decrease with rising temperature, since the chemical reaction velocity increases almost without exception with rising temperature.

In a similar manner the cathodic polarisation, which in these experiments always accompanies that at the anode, can be explained. When the current passes, the free ions separate, which must, in the state of equilibrium, according to the law of mass action, always be present in addition to the hydrated ones. Consequently a diminution in concentration and then polarisation follows, owing to the insufficiently great speed of the formation of free from hydrated ions. Indeed, the simultaneous occurrence of polarisation at the anode and the cathode finds a satisfactory explanation in this hypothesis, for both result from the same reaction: ion-hydrate $\rightleftharpoons$ ion + water, which

takes place at both electrodes in opposite directions, and any catalytic influence, such as the quoted case of the addition of strychnine, must change the velocity of the reaction in either direction in the same proportion. Indeed, as has been pointed out, a simultaneous increase of polarisation was always observed at the two electrodes.

In addition to this cause, another can be considered in the case of cathodic polarisation; we may expect that the discharged metallic ion frequently does not separate as solid metal, but remains at first dissolved, forming a supersaturated solution. With increasing supersaturation polarisation must increase.

The absence of polarisation of the mercury and lead compounds points to the fact that in these cases the chemical and physical processes concerned take place with greater velocity.

It should be expressly understood that all the foregoing experiments were carried out under such conditions that the metals dissolve without evolution of oxygen under the action of equal currents according to Faraday's law, and further that polarisation is not occasioned by any ohm-resistance at the electrodes. Were this the case, polarisation would immediately disappear on breaking the current, whereas a gradual decline was actually observed, which could easily be followed and measured; in other words, the above-mentioned systems, which before the passage of the current possessed no e.m.f. and were unable to give a current, could do so after having first passed a current and then broken it. Hence it was proved that both at the anode and at the cathode, which could be separately examined, a condition was brought about which, at the cessation of the current, had electromotive power.

(NOTE.—The same explanation holds for the supertension which occurs at the electrodes with liberation of gas, which also has electromotive power. I mention this because recently J. W. Richards—*Trans. Faraday Soc.*, 1913, ix., 140—has erroneously attempted to characterise this supertension merely as resistance).

If we account for the polarisation here observed by this explanation of failing reaction velocity, we can go a step further and apply the same explanation to the phenomena of passivity. With passive metals ionic hydration occurs so slowly at the anode (a certain amount of solution nearly always takes place), that the concentration of free ions, and therefore the potential difference, becomes so great in a short time that visible separation of the negative radical or of oxygen can result. Qualitatively these phenomena present nothing fresh in distinction to those described before; quantitatively they are only of value when chemical polarisation has become so strong that solution of the metal practically ceases and the negative radicals (or oxygen) are separated and become visible.

From this point of view we must henceforth understand by passivity phenomena all such as result from chemical polarisation. We have seen that passivity is not the exception but the rule, and that it is not connected with oxygen-containing anions, as was supposed, but that it takes place also with chlorides and other solvents, and especially that it can also take place at the cathode.

Briefly it may be mentioned that one may ascribe the peculiar shift in valency which occurs on dissolving many metals, e.g., chromium, by altering the experimental conditions, also to the changing hydration velocity of the ions of different valency.

I have thus attempted to establish as a fact that passivity phenomena are to be traced to those of reaction velocity. The reaction velocity theory can as yet afford no special information upon the conditions under which a metal becomes active or passive. Still one cannot reasonably regard this circumstance as a defect of the theory; it is rather due to the fact that our knowledge of the effect in chemical reaction velocities of outside factors is extraordinarily deficient. Thus another wide field is opened up for special research, and the work is being carried out with assiduity.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

THE UBIQUITY OF BORON.

The rarest metals and metalloids are to be found normally in the human organism, in the tissues of animals and vegetables. But the study of these bodies has been most difficult, and it is only quite recently that Prof. Armand Gautier has been able to discover and measure the tiny quantities of fluorine contained in the organs of man. M. Gabriel Bertrand, the head of one of the services of the Pasteur Institute, has just discovered that the tissues of plants and animals contain pretty appreciable quantities of boron or boric acid. And the quantitative method that he has devised in collaboration with M. Agulhon, to recognise the quantities of boron contained in divers substances, will have very important bearings on the application of the law against fraud and adulteration of food in trade. As people were ignorant of the constant presence of boron in the form of borate or some other combination in the living cellules, it was generally admitted that the boric acid found in the ashes of alimentary substances derived from plants or animals proceeded from a voluntary introduction as an antiseptic. As the dosage of this boric acid presented great difficulties, the mere qualitative research was all that was sought after; the result of this was that, up till now, the decision of the expert analytical chemist has depended almost exclusively on the greater or less degree of sensibility of the qualitative method that was employed. This way of operating is no longer admitted. The method of M. Bertrand enables one, in a few hours, to no longer confound the boric acid contained normally in the ashes of an alimentary substance with that which may have been introduced as an antiseptic. MM. Bertrand and Agulhon have thus found in a kilogram of the pulp of dried apricots 112.6 mgrms. of boric acid. In the same conditions they have calculated that there were 112 mgrms. per dry kilo. of the pulps of cherries, of dried figs, of strawberries, of peaches, of prunes, and in certain vegetables, such as carrots, French beans, turnips, and onions. Fifty-six mgrms. of boric acid are to be found per kilo. in English pears, black plums, apples, wild strawberries, white grapes, tomatoes, dried haricots, &c. In black grapes 225 mgrms. of boric acid have been found per kilogram. Lastly, these two scholars have found a smaller quantity of boric acid in the muscles of the rabbit, of the lobster, of the horse, of the ox, of the pigeon, in cows' milk, and even in the egg of a hen. Like arsenic, boron is then to be found everywhere. Many shopkeepers and tradesmen have been condemned because boric acid had been found in tinned goods. In the greater part of these cases they were simply judicial errors. Henceforth it will be easy, thanks to the method of M. Bertrand, to discover and recognise which are the fraudulent goods.

ANTITYPHOID VACCINATION.

The administration of microbial products by the gastric canal, in view of obtaining a vaccinal immunisation against the corresponding affection has already tempted several experimenters. Against typhoid fever, Schitchkine has had cultures of typhic bacilli, heated to 60 degrees, injected into rabbits without succeeding in vaccinating them. Prof. Courmont and Dr. Rochaix have obtained a relative immunity of the animals treated with pretty strong reactions which caused them to abandon the method. MM. Auguste Lumière and Jean Chevrotier, of Lyons, have succeeded, after a year's study, in preparing sterilised vaccines, then heated to fifty degrees, containing three microbial species in the proportion of 300 millions of Eberth's bacilli for 180 millions of coli bacilli and 120 millions of paratyphic bacilli. This vaccinal powder at the dose of three millions of micro-organisms per animal kilo. ingested in three fractions in an interval of eight days realised in guinea pigs and rabbits a sure and lasting

immunisation against typhic or paratyphic infection. Four months after their vaccination, the animals vaccinated were able to receive a mortal dose of each of the virulent cultures without showing any trouble whatever.

THE ELECTION OF PROF. CHARLES RICHEL.

Prof. Charles Richet has been elected a titular member in the section of medicine and surgery of the Academy of Sciences, in the place of the late Dr. Just Lucas Championnière. The section had presented M. Charles Richet in the first line, and in the second line according to their alphabetical order, Messrs. Bazy, Delorme, Pozzi, Quiem, and Reclus. After the first ballot, M. Charles Richet was proclaimed elected with 42 votes out of 56 voters, M. Reclus received 11 votes, M. Delorme 2, and M. Quiem 1 vote. The new Academician is a savant of the first rank. A few weeks ago he received the Nobel prize of Medicine for the year 1913, and only a few days ago the Government presented him with the scarf of a commander of the Legion of Honour. Yesterday he was appointed member of the Academy of Sciences. The son of a noted surgeon, member of the Institute and Professor of the Faculty of Medicine, Prof. Charles Richet was born in Paris in 1850. "Agrégé," or fellow of the Faculty, in 1879, he was appointed in 1887 to the chair of physiology at the Faculty of Medicine. He began to attract the attention of the learned world by the discovery of seropathy. It is, indeed, to M. Charles Richet that we owe the discovery of serums, the numerous victories of which are now well known. The first injection of serum into a man was made by the learned physiologist on December 6th, 1890. Before this, in 1888, he had tried an antituberculous serum on dogs, but without success. The second discovery due to Prof. Richet, a discovery which is revolutionising medicine and physiology, is that of anaphylaxis. In his speech, not yet published, pronounced at Stockholm in December last, M. Charles Richet made known his latest works in connection with this new road opened in the domain of serums and vaccines. It is known that anaphylaxis is a particular sensibility of the organism of animals to inoffensive doses of toxic substances especially of an albuminoid nature. Dogs having received a first injection of poison as a non-mortal dose were again injected with a small dose, three weeks or a month later. An unexpected fact then took place. Instead of being accustomed to the poison the organism of these animals had become so sensitive that this minimum dose had most terrible consequences and even occasioned rapid death. Anaphylaxis is then the contrary of nuthridatism or the custom or habit of poisons. The literary and dramatic production of the learned physiologist is important. His philosophical works, such as "Love and Intelligence," his "Essay of General Psychology," his theatrical pieces such as "Socrates and Circe," his novels "Sister Marthe," the "Pain of Others," "The Search for Happiness," &c., show that M. Charles Richet is a fine and delicate "lettré."

Institute of Chemistry.—Pass List January Examinations, 1914.—Of eighteen Candidates who presented themselves for the Intermediate Examination, seven passed:—H. G. T. Boorman, G. A. Bracewell, R. O. Eames, J. W. Harris, D. G. Hoyle, R. G. Thin, J. Young. One Candidate presented himself for Examination in General Chemistry for the Associateship and passed:—E. Spencer. Of twenty Candidates who presented themselves for the Final Examination for the Associateship (A.I.C.), ten passed:—In Branch (a), Mineral Chemistry—E. D. Goddard, F. C. Guthrie, G. S. Heaven. In Branch (c), Physical Chemistry—C. W. James. In Branch (d), Organic Chemistry—R. S. G. Knight, S. I. Levy, E. Williams. In Branch (e), the Chemistry of Food and Drugs, Fertilisers and Feeding Stuffs, Soils, and Water—B. G. Fagan, W. Honneymann, Miss Ethel G. Mocatta.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, January 22nd, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Heat Production Associated with Muscular Work: A Note on Prof. F. S. Macdonald's Paper, *Proc. Roy. Soc.*, B, vol. lxxxvii." By R. T. GLAZEBROOK, F.R.S., and D. W. DYE, B.Sc.

Prof. Macdonald's results are analysed graphically by plotting, equations being obtained from curves connecting the various quantities—Heat Produced, Work Done, Mass of Individual. The average values of Heat Produced by various persons, all working at the same rate, are first plotted against Rate of doing Work; a linear relation is found, of form $H = H_0 + \frac{W}{\lambda}$, where H_0 represents Heat Produced for zero Work Done.

The values of Heat Produced are next plotted against Rate of Work for each individual; these give approximate straight lines of the same equation as above, but with constants H_0 and λ differing for each individual. These values of λ are then plotted against corresponding masses M of individuals, and again a linear relation results, of the form $\lambda = a + bM$. In a similar manner H_0 is plotted against M , giving once more a linear relation $H_0 = a + bM$.

Collecting these equations, a complete expression connecting the quantities H , W , M , is found, viz., $H = a + bM + \frac{W}{a + bM}$. A table and series of curves give values of H by this equation for particular values of M and W used in experiments. These give good agreement with observed values of H .

"Chemical Interpretation of some Mendelian Factors for Flower Colour." By M. WHELDAL and H. L. BASSETT.

These researches deal with the Mendelian factors for flower-colour in varieties of *Antirrhinum majus*. Two varieties, ivory and yellow, are chiefly considered. Ivory is a simple Mendelian dominant to yellow and contains a factor "I" which is absent from yellow. The authors have previously identified the pale yellow pigment of the ivory variety with a flavone, i.e., apigenin. In the present paper it is shown that the yellow variety contains, in addition to apigenin, another flavone pigment, i.e., luteolin, which is present in the epidermis and which accounts for the deeper yellow colour of the flower. Hence the dominant ivory factor may be expressed as the power to inhibit the formation of luteolin in the epidermis.

The authors also criticise the hypothesis brought forward by Keeble, Armstrong, and Jones (*Proc. Roy. Soc.*, 1913, B, lxxxvii., 308) to account for the loss of colour both in an alcoholic solution of anthocyanin and in petals containing anthocyanin when immersed in alcohol, and the subsequent recovery of colour under various conditions. The above hypothesis postulates the existence in the petals of an oxydase and a reducing agent; the former produces anthocyanin from a colourless chromogen and the latter reverses the reaction. In the absence of water, i.e., in alcohol, the oxydase is rendered inactive, but the reducing agent remains active, and the colour disappears; on addition of water, the oxydase activity is restored and the colour returns.

The authors show that the colour can be restored either to petals or solution by dry hydriodic acid gas. Also the colour returns in water in an atmosphere of hydrogen. Moreover on dilution with water, the colour is restored to the strong alcoholic solution (which presumably does not contain oxydase) after it has been heated to 100°C.

"Determination of the Minimum Lethal Dose of Various Toxic Substances and its Relationship to the Body Weight in Warm-blooded Animals, together with Considerations Bearing on the Dosage of Drugs." By Prof. G. DREYER, M.D., and E. W. A. WALKER, M.D.

1. In warm-blooded animals of same species but different weights, dosage must be calculated in relation to body surface.

This result agrees with the conclusion already reached by Moore though on different grounds.

2. This statement is to be explained on the ground that concentration in plasma of any given substance administered is dependent on volume of blood circulating, which is itself proportional to body surface in any given species of animal.

3. It follows that in accurate measurement and standardisation of toxic substances and antitoxins it will now be possible to make use of animals of different weights within a given species instead of using only animals of an arbitrarily selected weight, as has hitherto been necessary.

4. Results in dosage calculated from one species of animal cannot directly be applied to another species merely by taking surface into due consideration, since tolerance and intolerance are specific characters shown to be in many cases independent of size of species concerned.

5. For the human subject, dosage, in relation to surface, works out very simply as, approximately:—

At 21 years ..	Full dose	At 3—4 years ..	$\frac{1}{2}$ dose
At 15 years ..	$\frac{2}{3}$ dose	At 1 year ..	$\frac{1}{4}$ dose
At 9—10 years	$\frac{1}{2}$ dose	In early months..	$\frac{1}{10}$ dose

"Experiments on the Restoration of Paralysed Muscles by Means of Nerve Anastomosis. Part II. Anastomosis of the Nerves Supplying Limb Muscles." By Prof. R. KENNEDY, M.D.

"Variations in the Sex Ratio of *Mus Rattus* following an Unusual Mortality of Adult Females." By F. NORMAN WHITE, M.D.

CHEMICAL SOCIETY.

Ordinary Meeting, December 18th, 1913.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 57).

340. "An Adiabatic Calorimeter." By FRANCIS WILLIAM GRAY.

The author described a water mantle, the temperature of which can be altered at will to prevent radiation inwards to or outwards from the calorimeter. The temperature is raised by pumping water from a hot bath through a flexible copper tube immersed in the water of the mantle. The temperature is lowered by passing tap-water through the same flexible copper tube, or, if necessary, by pumping water from a cold bath through the flexible tube. The flow of water is controlled by a system of two T-tubes and four taps. With this apparatus any rate of rise or fall of temperature likely to be required in thermochemical work can be obtained. A turbine stirrer is used for the mantle water.

341. "The Distillation of Coal in a Vacuum." By MAURICE JOHN BURGESS and RICHARD VERNON WHEELER.

An account was given of distillations of coal in a high vacuum at low temperatures, and the apparatus used described.

The gaseous products of distillation only were discussed in detail, the liquid products being dealt with in a subsequent paper.

The sequence of events when coal is gradually raised in temperature in the absence of air was described, and it was shown that of part of the coal substance a decomposition point occurs at about 350°.

Fractionation of the gases by means of liquid air and solid carbon dioxide dissolved in ether was stated to have enabled propane and butane to be isolated, and the presence of pentane established by explosion analysis.

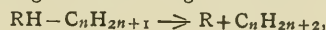
342. "The Composition of Coal." By DAVID TREVOR JONES and RICHARD VERNON WHEELER.

An account was given of an examination of the liquid products of distillation of coal in a vacuum at low temperatures, from which conclusions were drawn regarding the composition of the "resinous substances" that form part of the coal conglomerate.

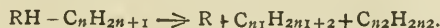
A description was given of the various compounds contained in the oils obtained, which consisted largely of unsaturated (ethylenic) hydrocarbons, naphthenes, paraffins, phenols (chiefly cresols and xylenols), and homologues of naphthalene. Benzene, anthracene, and solid aromatic hydrocarbons were stated to be absent.

The presence or absence of free hydrocarbons in any quantity in coal was discussed, and an hypothesis put forward to account for the rapid formation of paraffins, naphthenes, &c., on distilling coal at low temperatures. It was suggested that such hydrocarbons must be present in the coal substance in such a manner that whilst, in a sense, structurally complete, some change in their state, such as can be produced by moderate heating, must take place before they can be set free.

This hypothesis, particularised for the case of the paraffins, assumes their existence in coal as alkyl groups attached chemically to another non-alkyl group, R·H, the paraffin being in what can be termed a "bound" condition, as a component part of a molecule represented by the general formula $RH-C_nH_{2n+1}$. The rapid distillation of "free" paraffins from these "bound" molecules when coal is decomposed thermally was then explained according to the following scheme:—



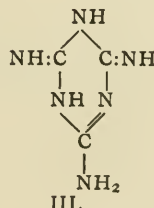
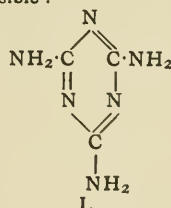
or—



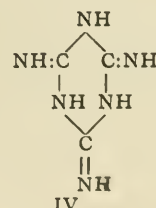
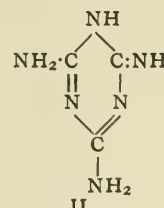
With certain modifications the hypothesis was used to explain the appearance of naphthenes, olefines, and naphthalene homologues in coal distillates.

343. "isoMelamine." (Preliminary Note). By HANS KRALL.

Four isomerides of melamine are theoretically possible:—



III.



Only one of these, usually assumed to be (I.), is known. Two series of alkylmelamines are known, and are usually assumed to be derived from (I.) and (IV.). During an investigation of the action of heat on guanidine salts, a second melamine has now been obtained; it is probably formed by the polymerisation of cyanamide in its carbodiimide phase, $NH_2C:NH$, and may be assumed for the present to be the hitherto unknown isomelamine (IV.).

When guanidine carbonate is heated for three hours at 180°, the residue consists of a mixture of ammeline and a substance which analysis shows to be isomeric with melamine. The former is readily dissolved by cold aqueous sodium hydroxide.

isoMelamine crystallises from water in ill-defined crystals, quite unlike the characteristic prisms of its isomeride. The two substances can be crystallised side by side from the same solution, so that the difference is constitutional, and not merely crystallographic.

isoMelamine gives rise to a chloride, nitrate, and sulphate of melamine, so that strong acids cause isomerisation. The true *acetate* can be obtained from which alkalis regenerate unaltered *isomelamine*.

Alkalis do not affect the constitution, but they induce hydrolysis more rapidly than with the normal isomeride.

At about 260° the compound decrepitates, and passes into the more stable form.

Both compounds are being further studied.

344. "Fluorone Derivatives. Part II. *Resorcinol-bezein*." By FRANK GEORGE POPE.

Resorcinol benzein, as prepared by Doebner's method, consists essentially of 3-hydroxy-9-phenylfluorone. Confirmation of this result was shown by its conversion into the sodium and barium salts, and by the preparation of the acetyl derivative, whilst by the action of phosphorus pentachloride it yields 3:6-dichloro-9-phenylxanthionium chloride identical with the product of the reaction between 3-hydroxy-9-phenylfluorone and phosphorus pentachloride. The different varieties of resorcinol benzein as described by H. v. Liebig (*Journ. Prakt. Chem.*, 1912, [ii.], lxxxv., 97, 241) were not obtained, neither were the anhydro-compounds described by the same author in 1908 (*Ibid.*, lxxviii., 534).

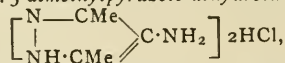
345. "The Relation between Viscosity and Chemical Constitution. Part VIII. Some Homologous Series." By ALBERT ERNEST DUNSTAN, FERDINAND BERNARD THOLE, and PERCY BENSON.

The authors have continued their work on the additive nature of log. viscosity, and have examined the viscosity of ninety-three compounds drawn from the homologous series of the fatty acids, alcohols, ethyl and methyl esters of the fatty acids, and esters of methylethylcarbinol, hexan- β -ol, heptan- β -ol, octan- β -ol, and undecan- β -ol.

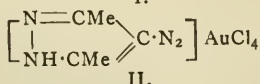
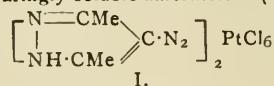
They find in each series that log. viscosity is additive within limits, but that the CH₂ differences vary with (1) association, (2) magnitude of the group to which the growing chain is attached, (3) molecular weight, (4) temperature.

346. "Non-aromatic Diazonium Salts. Part III. 3:5-Dimethylpyrazole-4-diazonium Salts and their Azo-derivatives." By GILBERT T. MORGAN and JOSEPH REILLY.

4-Amino-3:5-dimethylpyrazole dihydrochloride.



can be diazotised quantitatively to a stable, very soluble diazonium chloride, which has been characterised by conversion into the moderately soluble *platinichloride* (I.) and the sparingly soluble *aurichloride* (II.):—



Addition of sodium azide to the acid solution of diazonium chloride determines at once the liberation of diazo-nitrogen and the production of 4-triazo-3:5-dimethylpyrazole, a distinctly basic compound, which is precipitated only on neutralising the solution with sodium carbonate.

3:5-Dimethylpyrazole-4-diazonium chloride is even more stable than the corresponding salt from diazotised 4-aminoantipyrine; it is not readily decomposed by boiling aqueous potassium iodide, and its capacity for azo-coupling is retained after treatment with alkali carbonates, hydroxides, thiocyanates, and cyanides.

3:5-Dimethylpyrazole-4-azo- β -naphthol dissolves very sparingly in aqueous alkali hydroxides, but is insoluble in water.

3:5-Dimethylpyrazole-4-azo- β -naphthylamine is a pale orange-brown base.

347. "The Relative Activities of certain Organic Iodo-compounds with Sodium Phenoxide. Part IV. The Influence of the Solvent." By DAVID SEGALLER.

The velocity-coefficients of the reaction between sodium phenoxide and ethyl and propyl iodides have been measured with a view of studying the influence of the solvent in this reaction.

The following solvents were employed: methyl alcohol, ethyl alcohol, propyl alcohol, *isobutyl* alcohol, *isoamyl* alcohol, and acetone.

It was shown that there is no connexion in this reaction between the dielectric constant of the solvent and the influence of the latter on the rate of the reaction. The influence of the medium is very large, the velocity-coefficient in acetone solution being more than one hundred times as large as that in *isoamyl* alcohol solution.

348. "The Polysulphides of the Alkali Metals. Part I. The Polysulphides of Sodium." By ALEXANDER RULE and JOHN SMEATH THOMAS.

An investigation has been made of the action of sulphur on alcoholic solutions of anhydrous sodium hydrosulphide prepared by the method previously described by one of the authors (*Trans.*, 1911, xcix., 558). A vigorous reaction takes place between sulphur and the hydrosulphide in alcoholic solution, with the evolution of hydrogen sulphide and the formation of polysulphides.

Using amounts of sulphur corresponding with the di-, tri-, tetra-, penta-, and a possible hexa-sulphide, and concentrating the solution, a solid product was obtained, but only when the proportions of hydrosulphide and sulphur for the tetrasulphide were used was the product homogeneous. It consisted of the pure anhydrous tetrasulphide, which is a brownish-yellow substance, crystallising in well-defined cubes.

Below the proportions for the tetrasulphide, mixtures were obtained which contained unchanged hydrosulphide. At the pentasulphide stage the solid product is a mixture of the tetrasulphide and sulphur, whilst above that stage there is some indication of the separation of a higher polysulphide.

The course of the reaction and the probable nature of the substances present in solution before evaporation of the latter was determined by estimating the amounts of hydrogen sulphide evolved when varying amounts of sulphur were used in the reaction.

Anhydrous sodium disulphide was also obtained by reducing solutions of the tetrasulphide with metallic sodium. It is a bright yellow, micro-crystalline powder, less soluble in alcohol than the tetrasulphide.

349. "Nitro acids Derived from 2:3-dimethoxybenzoic Acid and 4-methoxyphthalic Acid." By JOHN CANNELL CAIN and JOHN LIONEL SIMONSEN.

5-Nitro-2:3-dimethoxybenzoic acid was prepared by nitrating 2:3-dimethoxybenzoic acid and also by nitrating 2:3-dimethoxytoluene and oxidising the 5-nitro-2:3-dimethoxytoluene formed.

6-Nitro-2:3-dimethoxybenzoic acid (Wegscheider and Klemenc, *Monatsh.*, 1910, xxxi., 709) was synthesised as follows:—3-Hydroxy-*o*-tolyl methyl ether on nitration yields 5:6-dinitro-3-hydroxy-*o*-tolyl methyl ether, which on methylation and reduction gives 2-nitro-5:6-dimethoxy-*m*-toluidine. On elimination of the amino-group the resulting 6-nitro-2:3-dimethoxytoluene furnishes, on oxidation, the required acid.

The nitration of 4-methoxyphthalic acid yields a mixture of 3- and 5-nitro-4-methoxyphthalic acids, which can readily be separated. The former was also synthesised by oxidising 1-nitro-2-naphthyl methyl ether, and the latter by oxidising 5-nitro 4-methoxy-o-xylene.

350. "The p-Nitrobenzoates of Borneol and isoBorneol." By GEORGE GERALD HENDERSON and ISIDOR MORRIS HEILBRON.

In the course of investigations on the action of oxidising agents on camphene and on bornylene, the authors have more than once had some difficulty in deciding whether an alcohol present among the oxidation products was borneol or isoborneol. It is troublesome to obtain these compounds in a state of purity by crystallisation alone, and such of their hitherto described derivatives as are well characterised and easily prepared, for example, the hydrogen phthalates, melt at the same or very nearly the same temperatures. The authors therefore sought for some derivative of borneol and isoborneol by means of which the alcohols could be more easily distinguished from each other, and ultimately found that the p-nitrobenzoates, which can be prepared and purified without difficulty, meet this requirement.

For the preparation of the p-nitrobenzoates the following method gives good results:—The calculated quantity of p-nitrobenzoyl chloride is added to a solution of the alcohol in ten to fifteen times its weight of pure pyridine, and the reaction, which starts immediately, is completed by warming the solution for an hour or two on the water bath. The pyridine is then removed by cautious addition of dilute sulphuric acid, the flask being kept cool during this operation by immersion in ice-water, and the precipitated p-nitrobenzoate is collected, washed with dilute sulphuric acid and with water, dried, and crystallised from alcohol. Usually one crystallisation is sufficient.

Borneol p-nitrobenzoate, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{17}$, crystallises from alcohol in minute, lustrous, colourless plates, which melt at 137° . It is sparingly soluble in cold alcohol, readily so in the other common organic solvents, and insoluble in water:—

0.472 gave 19.1 cc. N_2 (moist) at 13° and 754 mm. $\text{N} = 4.74$.

$\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}$ requires $\text{N} = 4.62$ per cent.

isoBorneol p-nitrobenzoate separates from alcohol in fine, colourless needles, which melt at 129° . In solubility it closely resembles the corresponding borneol ester:—

0.559 gave 22.5 cc. N_2 (moist) at 12° and 760 mm. $\text{N} = 4.78$.

$\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}$ requires $\text{N} = 4.62$ per cent.

The ultra-violet absorption spectra of these esters were found to be identical, each compound, in $\text{M}/10,000$ -solution, showing a shallow band with head at $1/\lambda$ 3080.

The esters are readily hydrolysed when heated with dilute aqueous sodium hydroxide under reflux. The liberated alcohols were distilled in a current of steam, collected, dried, and crystallised from light petroleum. The purified borneol was found to melt at 208° and the isoborneol at 217° ; the melting point of the former is the same as, but that of the isoborneol three degrees higher than, that formerly recorded.

351. "The Identity of the Supposed β -2 : 5-Dimethylpiperazine." By WILLIAM JACKSON POPE and JOHN READ.

The authors have continued the examination of the substances described as α - and β -2 : 5-dimethylpiperazine, and now show that the behaviour of the β -isomeride can only be explained on the assumption that it is *cis*-2 : 4-dimethylpiperazine; it is further concluded that the α -compound is *trans*-2 : 5-dimethylpiperazine.

252. "Oxidation of the Anhydrides of 1 : 1-Dihydroxy-dinaphthylmethanes." (Preliminary Note.) By HEMENDRA KUMAR SEN-GUPTA.

This investigation has been undertaken with the object of ascertaining the constitution of some of the

condensation products of α -naphthol with ketones, as also of synthesising some naphthanthrone derivatives. The anhydride of β -1 : 1-dihydroxydinaphthylpropane, $\text{CH}_3 > \text{C} < \text{C}_{10}\text{H}_6 > \text{O}$, yields, on oxidation by chromic acid, two products, namely, (i.) an orange compound, $\text{C}_{24}\text{H}_{16}\text{O}_3$, crystallising in thin, soft needles, and melting at 287° ; and (ii.) a golden-yellow compound, $\text{C}_{24}\text{H}_{16}\text{O}_4$, crystallising in lozenges and melting at 245° . The latter gives on reduction a dihydroxy-derivative, $\text{C}_{24}\text{H}_{18}\text{O}_3$ (m. p. 252 — 253°); its diacetyl derivative crystallises in needles and melts at 241 — 242° . The anhydride of γ -1 : 1-dihydroxydinaphthylpentane, $\text{Et} > \text{C} < \text{C}_{10}\text{H}_6 > \text{O}$, similarly yields a deep red compound crystallising in plates and melting at 221° . The constitution of these products are being studied.

353. "The Relation of Uranous Salts to Thorium." By ALEXANDER FLECK.

If the electrons expelled in radioactive change arise from the same part of the atom in which the electrons governing electrochemical change of valency exist, it should follow that the chemical properties of the uranous and thorium ions are identical. By reducing a mixture of thorium and uranyl salts by nascent hydrogen and then treating the reduced liquid fractionally with a precipitant, it was found that although the properties of thorium and uranium in the quadrivalent condition are very similar, yet there is a distinct difference in their chemical nature, and they can be separated from one another by fractional precipitation. In carrying out the examination of their properties it was necessary that the precipitation, filtration, and other operations should be performed without air coming in contact with the reduced liquid.

As a result of these experiments the conclusion was drawn that the electric charges on the α - and β -particles must arise from the nucleus of the atom, and that electrons may be added to or withdrawn from the external ring of electrons, thereby increasing or diminishing the valency of the atom.

354. "The System: Xylene—Alcohol—Water." By ALFRED HOLT and NORMAN MURRAY BELL.

The authors have determined the data of the varying miscibility of xylene, alcohol, and water at different temperatures, also the position of the tie lines which give the composition of the conjugate solutions.

The extent to which xylene is separated from its solution in alcohol by the addition of water has also been examined, as also the composition of mixtures of the three liquids which possess the same specific gravity.

355. "Interaction of Glycerol and Oxalic Acid." By FREDERICK DANIEL CHATTAWAY. (This paper was read at the meeting on December 4th, 1913).

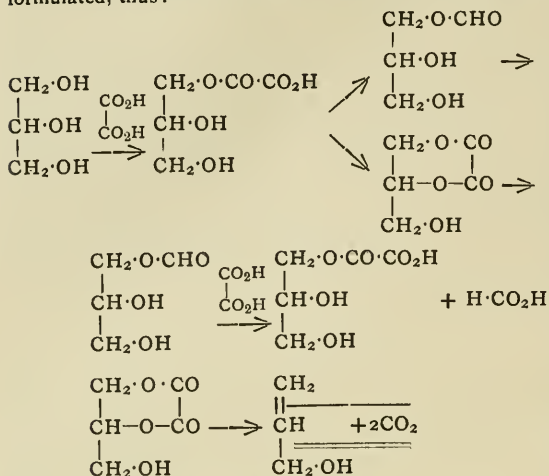
The explanation usually given in the text-books of the reactions occurring when glycerol and oxalic acid are heated together, and commonly employed in the laboratory preparation of formic acid and of allyl alcohol, is fundamentally incorrect.

The true explanation is the obvious one. The oxalic acid acts on glycerol as it does on other alcohols, and produces an acid and a normal oxalate. The former, like all such compounds, is unstable at a slightly elevated temperature, and decomposes when this is reached into carbon dioxide and monoformin. The fresh oxalic acid added displaces the formic acid from the latter, and the cycle of operations repeats itself.

The more complicated reaction which goes on when the first product of the interaction of glycerol and oxalic acid is rapidly heated, until evolution of carbon dioxide ceases and then at a much higher temperature recommences with simultaneous production of allyl alcohol, is the decomposition at the high temperature of the normal ester, which is produced from the acid ester by a repetition of the ester formation, into carbon dioxide and allyl alcohol.

The main reactions concerned in the production of

formic acid and of allyl alcohol should therefore be formulated, thus:—



and not as is at present invariably done.

NOTICES OF BOOKS.

Rays of Positive Electricity and their Application to Chemical Analyses. By Sir J. J. THOMSON, O.M., F.R.S. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

THE publication of this book has been awaited with great interest both by physicists and chemists who recognise the remarkable possibilities of Sir J. J. Thomson's new method of analysis, and the account of the work which has been done in the Cavendish laboratory during the past seven years will, it is to be hoped, induce many other workers to enter the new field of research. The method is in some respects more powerful even than spectrum analysis, and the technique is not specially difficult. In the book the experimental details and the apparatus employed are described, and some of the photographs which have been obtained are reproduced. Some account is given of the researches of Stark on the Doppler effect of positive rays, and of Gehrcke and Reichenheim's work on the positive rays starting from the anode, and the nature of X_3 , the substance giving the "3" line is shortly discussed. The author considers that the evidence points to the conclusion that X_3 is triatomic hydrogen H_3 , which appears to be more stable than any known allotropic form of an element.

Photo electricity. By H. STANLEY ALLEN, M.A., D.Sc. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

A HEARTY welcome will undoubtedly be accorded to this book, more particularly since, with the exception of Sir J. J. Thomson's "Conduction of Electricity through Gases," it is the only one dealing with photo-electricity which has been published in the English language. The author believes that further investigation in this sphere may lead to the reconciliation of the quantum theory with the undulatory theory of light, and he gives a quite unbiassed account of the phenomena and theories of photo-electricity. The book is written for fairly advanced students, and does not go into elementary details. An introductory chapter gives a very clear historical review of the whole field of research, and outlines the plan of the book. The work of Stark and Lennard on fluorescence and phosphorescence is fully treated for the first time in an English text-book, and the results of the work of the author and others upon photo electric fatigue is well summarised.

The Microscopic Analyses of Metals. By FLORIS OSMOND. Edited by J. E. STEAD, D.Met., F.R.S., F.I.C. Second Edition, revised and corrected by L. P. SIDNEY. London: Charles Griffin and Co., Ltd. 1913.

THE second English edition of this work is practically a reprint of the original translation with a few corrections of minor details, the author having expressed the wish shortly before his death that no fundamental alterations should be made in the text. Some fresh matter has, however, been added by the editors. This includes a translation of an essay by Osmond and Cartaud on polishing, and also some notes on the practical applications of metallography, and chapters on segregation in steel and on the macrostructure of steel, by Dr. J. E. Stead. The illustrations, which are an important feature of such a book as this, are very numerous and are well reproduced.

Seventh Annual Report of the Metropolitan Water Board. By Dr. A. C. HOUSTON.

THE seventh annual report on the results of the chemical and bacteriological examination of the London waters for the twelve months ended March 31st, 1913, contains abstracts of the important features of previous reports, and gives statistics of supply and short accounts of the research work which has been done in the Board's Laboratory. The Director has to report that the number of complaints from consumers showed a very marked increase as compared with those of previous years, and he admits that they were quite justifiable. They were confined almost entirely to districts supplied with water from the Staines reservoirs, where excessive development of *Tabellaria* frequently took place.

A New Era in Chemistry. By HARRY C. JONES. London: Constable and Co., Ltd. 1913.

THE author of this book has produced an interesting and pleasantly written account of the new era in chemistry, which he dates from the year 1887, when some of the most important work of van't Hoff and Arrhenius was first published. The author has already shown in earlier books that he possesses to a marked degree the faculty of making comparatively difficult subjects easily understandable by readers who do not possess a very deep knowledge of physics and chemistry, and in this book he gives a readable account of some of the most important developments in general chemistry in the last quarter of a century. He has had a personal knowledge of many of the men who have been instrumental in bringing about the new era, and had moreover the probably unique experience of working as a student under van't Hoff, Arrhenius, and Ostwald. Of these men, and of other great scientists, he gives many personal reminiscences and anecdotes, and the strong human note in the book will inevitably make it appeal to the student. From a scientific point of view the material is well chosen, and the short explanations appear to be always accurate and clear.

Reinforced Concrete Railway Structures. By J. D. W. BALL, Assoc. M.Inst.C.E., A.C.G.I. London: Constable and Co., Ltd. 1913.

THIS book contains a thoroughly practical exposition of the principles upon which the design and construction of structures made of reinforced concrete depend, and is intended more particularly for the use of the railway engineer. A special feature of the text is the great number of worked out examples, and the author has endeavoured to limit the formulæ given to those which are absolutely essential and to simplify them as far as possible, while the curve diagrams should greatly facilitate many calculations.

Organic Chemistry for Students of Medicine. By JAMES WALKER, LL.D., F.R.S. London: Gurney and Jackson. Edinburgh: Oliver and Boyd. 1913.

THIS book is intended for the use of students of medicine who are usually able to devote only a very short time to

the study of chemistry, and yet need to have a fairly detailed knowledge of some of the more complicated substances. In such circumstances much the best plan is for them to base their work upon a text-book such as this, in which substances of medical interest only are included. After a short chapter dealing with methods of determining melting-points and boiling-points, elementary analysis, &c., the author introduces the study of methane and some of its simple derivatives by a brief discussion of the distillation of wood. Thence he passes to a very short outline of the chemistry of the carbohydrates and alcoholic fermentation, and so on to more complicated compounds of the fatty series. In the same way the distillation of coal forms the introduction to the chapters on the aromatic derivatives. Nitrogen compounds are not introduced until the later part of the book. The division of the text into short sections does much to lighten the student's difficult task, and the brief discussions of the constitution and properties of various groups of important compounds such as alkaloids and proteins are admirably clear and quite sufficient for their purpose.

Handbook on Sanitation. By GEORGE M. PRICE, M.D. Third Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1913.

THIS book contains an outline of the theory and practice of sanitation, the latter being discussed entirely from the American point of view. It is divided into three parts, the first of which deals with sanitary science. In this part the chapter on ventilation has been entirely re-written in the third edition. The second part gives an account of the applications of the principles of sanitation, and the construction and sanitation of tenements, private houses, factories, &c., are described in it, while sections on the hygiene of foods and on disinfectants are included. The last part of the book deals with the duties of inspectors, but since England is decidedly ahead of America with regard to the training provided for inspectors and the qualifications required of them, this section will be of very little use to the English student.

Underground Waters for Commercial Purposes. By FRANK L. RECTOR, B.S., M.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1913.

THE mineral water trade of New York, although as yet only in its infancy, is gaining rapidly in importance and volume, and hence the author of this little book thought that it might be useful to compile an account of all the literature dealing with the use of underground waters and springs for commercial purposes which has been published recently in America. The book gives short outlines of the chemical, bacteriological, and microscopical examination of water. These descriptions are sufficiently full and clear to give the reader a good grasp of the general principles involved in the various operations, but are not detailed enough to be used as a guide to the actual work in the laboratory.

The Journal of the Society of Dyers and Colourists. December, 1913.

THIS journal contains a very interesting paper read before a joint meeting of the Manchester Sections of the Society of Dyers and Colourists and the Society of Chemical Industry by Mr. Julius Hübner on "The History of Dyeing." Every student of technology is the better for some knowledge of the history of his special branch, but cannot as a rule devote more than a very short time to the study, and a *résumé* such as this is invaluable for stimulating his interest in the development of modern theories and practice. The lecturer made a careful study of all the original publications to which he could get access dealing with the very early history of dyeing in the East and elsewhere, and gave some very quaint recipes and illustrations, closing his remarks with the end of the 17th century.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de France,
Vol. xiii.-xiv., No. 23, 1913.

Determination of Sulphates in Wine by Physico-chemical Volumetric Method.—Paul Dutoit and Marcel Duboux.—The volumetric determination of the sulphates in wine with $N/4$ -baryta as reagent, and determining the conductivities in order to ascertain the end-point of the reaction, is more accurate than the gravimetric method. It is not affected by the presence of salts of calcium, magnesium, &c., nor by tartaric or malic acids.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xvi., No. 14, 1913.

Boron Hydrides.—Alfred Stock, Kurt Friederici, and Otto Priess.—The following compounds of boron and hydrogen have been prepared:—1. B_2H_6 . Obtained by heating B_4H_{10} . Melting-point, -169° ; boiling-point, -87° . Very easily decomposed by water, otherwise stable. 2. B_4H_{10} . Obtained by fractionating the gas resulting from magnesium boride and acid. Melting-point, -112° ; boiling-point, $+16^\circ$. Very easily decomposes to give other boron hydrides. Slowly decomposed by water. 3. Liquid colourless fraction of tension about 20 mm./ 0° . Obtained like 1. Very unstable, polymerises to yellow solid compounds. Possibly contains B_6H_{12} . 4. B_6H_{12} . Like 2 from the raw gas. Tension 10 mm./ 0° . Very easily decomposed by water. 5. $B_{10}H_{14}$. Obtained like 1 and by heating B_2H_6 . Melting-point, 99.5° . Volatilises undecomposed. Soluble in CS_2 . Insoluble in water. Gives yellow solution with caustic soda. 6. Non-volatile colourless hydride, soluble in CS_2 . Obtained like 1. Probably contains 12 atoms of boron in the molecule. Stable towards water. Gives yellow solution with caustic soda. Gives 7 on heating. 7. Non-volatile yellow hydride, insoluble in CS_2 . Obtained like 1 and by heating 6. Contains about 4H atoms to 5 atoms of B. Dissolves undecomposed in water. 8. Liquid hydride which volatilises with difficulty. Obtained by heating 6. 9. Colourless, non-volatile hydride insoluble in CS_2 . Obtained by heating B_2H_6 ; gives white crystals with water, yellow solution with caustic soda. 10. Brown hydrides resembling boron, and poor in hydrogen. Obtained by heating 7 to a higher temperature. Nearly all these hydrides give new compounds when they react with water or alkalis. Thus boron resembles carbon in its power of yielding compounds.

Behaviour of Radio-elements towards Precipitants.—Kasimir Fajans and Paul Beer.—With very few exceptions a radio-element is precipitated from a very dilute solution with a precipitate of an ordinary element, when the precipitation takes place in conditions in which the radio-element would separate if it were present in a weighable amount. The fact that this rule holds good universally shows that the behaviour of the radio elements in precipitation reactions is much less affected by abnormal adsorption phenomena than has been supposed.

No. 15, 1913.

Arseno-stibino and Arsino-bismutho Compounds.—P. Ehrlich and P. Karrer.—Stibine oxides and dichlorides and other inorganic antimony salts of the trivalent metal readily react with arsines to give arseno-stibino compounds, and bismuth trichloride behaves similarly. The condensations occur very easily at the ordinary temperature when the methyl-alcoholic solutions are mixed. The arseno-stibino compounds are very stable, with properties resembling those of the arsenious derivatives. They are usually yellowish or dark brown. The bismuth compounds

are very unstable, and are decomposed when boiled with water. They are black in colour.

Quantitative Investigations of the Absorption of Ultra-violet Rays by Saturated and Unsaturated Ketones and Aldehydes of the Fatty Series.—Jean Bielecki and Victor Henri.—The absorption curves of aldehydes and ketones can be analysed into "elementary absorption curves." With the aldehydes two elementary curves are obtained, one corresponding to the carbonyl and the other to the alkyl. With the ketones three curves are obtained, namely, the same elementary curve of the carbonyl and two curves corresponding to the two alkyls. In the absorption of rays of different wave-lengths the electrons sometimes of one of the atomic groups, and sometimes of another, come into play. The absorption is produced by only one part of the whole molecule, and this part alters with the wave-length.

Atti della Reale Accademia dei Lincei.

Vol. xxii. [ii.], No. 9, 1913.

Compounds of CdSO_4 with Li_2SO_4 , Na_2SO_4 , K_2SO_4 .—G. Calcagni and D. Marotta.— CdSO_4 forms no compound with Li_2SO_4 . With Na_2SO_4 it gives three compounds, viz.:— $3\text{CdSO}_4 \cdot \text{Na}_2\text{SO}_4$, $\text{CdSO}_4 \cdot \text{Na}_2\text{SO}_4$, and $\text{CdSO}_4 \cdot 3\text{Na}_2\text{SO}_4$. With K_2SO_4 it forms two compounds, both previously unknown, $3\text{CdSO}_4 \cdot \text{K}_2\text{SO}_4$ and $2\text{CdSO}_4 \cdot \text{K}_2\text{SO}_4$.

Phototropism of Hydrazones.—F. Bovini.—The author has prepared the following hydrazones:—Phenyl, *p*-tolyl, *β*-naphthyl, and diphenyl hydrazones of acetophenone; phenyl, *p*-tolyl, *β*-naphthyl, diphenyl, methyl-phenyl, and benzylphenyl hydrazones of benzophenone. None of these is phototropic, and apparently the presence of an aldehyde hydrogen is necessary in order that a hydrazone may exhibit phototropism. The phenomenon is not manifested if the hydrogen is replaced by any radicle.

MISCELLANEOUS.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 2nd inst., the Duke of Northumberland, K.G., President, in the Chair. The Right Hon. Lord Avebury, Mr. H. A. Humphrey, Dr. Gerald Moody, and Mr. A. Ross were elected Members. The special thanks of the Members were returned to Lady Huggins for her present of a portrait of the late Sir William Huggins, and to Mr. Bence Jones for his present of three boxes containing some relics of Faraday. The Honorary Secretary announced the decease of Sir David Gill, K.C.B., and Mr. H. F. Makins, Members of the Royal Institution, and resolutions of condolence with the relatives were passed.

Institute of Chemistry.—Mr. William MacNab, F.I.C., will deliver the first of two lectures on "Explosives," on Thursday, February 26, 1914, at 8 p.m., at King's College Strand. *Syllabus of Lecture*:—Short historical sketch of manufacture and use of explosives; comparatively little change or progress made until about fifty years ago; since then great and varied development. Field of available bodies and mixtures as explosives greatly widened by introduction of detonators. General considerations of the character of explosive decompositions. Two modes of explosion—combustion or deflagration and detonation; means of initiating each mode. Velocity of explosion wave in detonated explosives. Conditions under which the result of an explosive decomposition can be foreseen from theory; conditions which interfere with theoretical conclusions and necessitate experimental determination. Limitations of experimental methods. Heat developed, volume and composition of gases, and pressure produced; effect of pressure on composition of gases. Theoretical temperature reached on explosion; experimental attempts to measure it; need for further work. Sensitiveness of explosives—means of increasing or diminishing it. Con-

sideration of certain types of explosives in general use. Qualities which they should possess. Methods of testing explosives.

South-Western Polytechnic Institute, Manresa Road, Chelsea, S.W.—A course of six lectures "On Milk," followed by practical work, will be delivered by Prof. A. Harden, D.Sc., F.R.S. (of the Lister Institute), on Thursday evenings at 7.30 o'clock, commencing February 5, 1914. The syllabus is as follows:—*Chief Properties of Milk*.—The Constituents of Milk; Milk-sugar, Fat, Proteins, Salts; Specific Gravity; Analysis of Milk; Detection of Adulteration; Effect of Heat on Milk; Dietetic Value of Milk, *Bacteria in Milk*.—General Life History of Bacteria; Methods of Detection, Enumeration, and Isolation; Mode of Reproduction and Nutrition; Occurrence in Air, Water, and Soil, and in the Animal Body; the Nature and Source of the Bacteria in Milk; Suspended Matter in Milk; Bacteriological Standards of Purity. *Changes Produced in Milk by Bacteria*.—Curdling of Milk by Acid and by Rennet; Influence of Temperature and Preservatives. *Spread of Disease by Milk*.—Diphtheria; Scarlet Fever; Typhoid; Summer Diarrhoea; Tuberculosis; Tracing of Epidemics to Milk Supply. *Preventive Measures*.—Importance of Cleanliness; Refrigeration; Methods of Distribution; Sterilised and Pasteurised Milk. *Practical Work*.—A Practical Class will be held immediately after the lecture, the work of which will include simple methods of ascertaining the Composition of Milk, the Detect on of Impurities and Preservatives in Milk, and the Bacteriology of Milk.

MEETINGS FOR THE WEEK.

- TUESDAY, 10th.—Royal Institution, 3. "Animals and Plants under Domestication," by Prof. W. Bateson, F.R.S., &c.
WEDNESDAY, 11th.—Royal Society of Arts, 8. "History of Colour Printing," by R. A. Fiedie.
THURSDAY, 12th.—Royal Institution, 3. "Types and Causes of Earth Crust Folds," by Prof. Sir T. H. Holland, F.R.S.
— Royal Society of Arts, 4.30. "Khorasan, the Eastern Province of Persia," by Major Percy Molesworth Sykes, C.M.G., &c.
— Royal Society. "Chemical Action that is Stimulated by Alternating Currents," by S. G. Brown. "Effect of the Gangetic Alluvium on the Plumb-line in Northern India," by R. D. Oldham. "Origin of Black Body Radiation," by G. W. Walker. "Transmission of Electric Waves along the Earth's Surface," by H. M. Macdonald. "Transparency or Translucence of the Surface Film produced in Polishing Metals," by G. T. Beilby. "Method of avoiding Inaccuracy due to Weight Errors in 'Fixing' a Gold Coinage Standard Trial Plate," by A. O. Watkins. "A Thermomagnetic Study of the Eutectoid Transition Point of Carbon Steels," by S. W. J. Smith and J. Guild. "Note on Osmotic Pressure," by W. K. Bousfield.
FRIDAY, 13th.—Royal Institution, 3. "Production of Neon and Helium by Electric Discharge," by Prof. J. Norman Collie, F.R.S., &c.
— Alchemical Society, 8.15. (At International Club, Regent Street, S.W.). "Some Notes on the Doctrine of the First Matter, with special reference to the Works of Thomas Vaughan," by Sijil Abdu-Alli.
SATURDAY, 14th.—Royal Institution, 3. "The Electric Emissivity of Matter," by J. A. Harker, F.R.S., &c.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

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The next INTERMEDIATE EXAMINATION.

will commence on TUESDAY, MARCH 24, 1914.
FINAL EXAMINATIONS in—(a) Mineral Chemistry, (b) Metallurgical Chemistry, (c) Physical Chemistry, (d) Organic Chemistry, and (e) the Chemistry of Food and Drugs, &c., will commence on MONDAY, MARCH 23, or on MONDAY, MARCH 30, 1914.
The LIST of CANDIDATES will be CLOSED on TUESDAY, FEBRUARY 24, 1914.
Forms of application and further particulars can be obtained from the REGISTRAR, Institute of Chemistry, 30, Bloomsbury Square, London, W.C.

APPOINTMENTS REGISTER.

A Register of Fellows and Associates of the Institute of Chemistry who are seeking appointments is kept at the Offices of the Institute.

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THE ESTIMATION AND DISTINCTION OF OZONE, NITROGEN PEROXIDE, AND HYDROGEN PEROXIDE AT HIGH DILUTIONS.

By J. N. PRING, D.Sc.

THIS research was undertaken with a view of establishing some method whereby an analytical estimation and distinction of these gases could be made when present in very small quantities. The immediate purpose for which this method was required was in order to make analyses of air at high altitudes for these substances. It was necessary to employ some stable reagent which would react rapidly and quantitatively with these gases, and which could be used in small vessels attached to balloons, and also applied in mountain districts.

No conclusive method has yet been devised which would satisfy these requirements.

After a number of experiments it was found that a concentrated aqueous solution of pure potassium iodide was the only reagent which gave satisfactory results in determining ozone and nitrogen peroxide, while the use of titanium sulphate in sulphuric acid was the only satisfactory means of detecting traces of hydrogen peroxide.

It was found that the potassium iodide solution reacts with ozone, even when the gas is present at high dilutions, with great rapidity. This is also the case at temperatures as low as -50° , when the gas is passed over the surface of the solid reagent. As the reaction which takes place between ozone and potassium iodide is known to be very complex, the conditions were investigated for the distinction of this gas from other possible reacting gases which are present in the atmosphere.

A. Action of Ozone on Potassium Iodide.

It has been found that in a neutral solution this reaction gives rise to a large number of substances, including free iodine, potassium hypoiodite, iodate, periodate, hydrate, and peroxide (cf. Garzaroli-Thurnlackh, *Monatsh.*, 1901, xxiii., 955; Bruck, *Ber.*, 1900, [2], xxxiii., 1832; Pechard, *Comptes Rendus*, 1900, cxxx., 1705).

An estimation of hypoiodite and free iodine, on the one hand, can be made in presence of the other compounds by titrating with sodium thiosulphate. If the solution is then acidified, the iodate and periodate are decomposed with liberation of iodine, and are thus readily estimated by again titrating this with thiosulphate. In the present work the measurements thus obtained were later compared with those given by hydrogen peroxide and nitrogen peroxide.

Ozonised oxygen was prepared by heating potassium permanganate in a combustion tube, and, after drying, passing the oxygen generated through Siemens tubes, and then collecting over distilled water in a gas holder of 10 litres capacity. Before filling with oxygen the whole apparatus was first carefully exhausted so as to ensure the absence of nitrogen and water vapour.

Measured volumes of this gas were then passed through, or over the surface of, the reagent, consisting of equal weights of potassium iodide and water contained in a small wash-bottle. The resulting solutions were then analysed by titration with N/100 or N/1000 sodium thiosulphate, and, after removal of the free iodine, the iodate was estimated as described above. The potassium hydrate was estimated in a separate sample by titration with N/1000 sulphuric acid.

Experiments were made with the gas at different concentrations by progressively diluting the gas in the holder by means of air which was drawn through a hot alkaline

TABLE I.—Reactions at Room Temperature.

Volume of gas (cc.).	Conc. of ozone, volume per cent.	Mgms. equiv., calculated on total volume of reagent.			Ratio, free I_2 to I_2 as iodate
		Free iodine (+KIO).	Iodine as iodate (+periodate).	Potassium hydrate.	
10	4.03	0.0105	0.0255	0.009	1 : 2.4
After standing 12 days		0.0137	0.024	Nil	
5	2.86	0.0052	0.00755	Nil	1 : 1.5
100	2.17	0.0438	0.150	0.028	1 : 3.5
After standing 12 days		0.0633	0.168	0.006	
4000	1.4	0.127	5.0	0.015	1 : 39.2
1000	0.90	0.288	0.570	0.012	1 : 2.5
After standing 15 hours		0.331	0.492	0.026	1 : 1.4
50	0.49	0.0066	0.0152	0.0048	1 : 2.3
After standing 12 days		0.0077	0.0142		
500	0.20	0.054	0.037	0.001	
2000	0.10	0.120	0.073	0.007	1 : 0.60
After standing 15 hours		0.183	0.074	0.008	1 : 0.41
150	0.02	0.0028	0.00047	Nil	1 : 0.16
After standing 12 days		0.0019	0.0016	Nil	
1000	0.016	0.012	0.0027	0.008	1 : 0.23
After standing 12 days		0.014	0.0032	Nil	
6500	0.00062	0.0040	Nil	Nil	1 : 0

TABLE II.—Reaction at Low Temperatures.

Temp. of reagent.	Volume of gas (cc.).	Conc. of ozone, volume per cent.	Mgms. equiv., calculated in total volume of reagent.			Ratio free I_2 to I_2 as iodate.
			Free iodine (+KIO).	Iodine as iodate (+KIO4).	Potassium hydrate.	
-22°	4000	0.014	0.041	0.011	0.008	1 : 0.27
-28°	6000	0.0085	0.006	0.040	0.001	1 : 6.7
-53°	6500	0.0027	0.0027	0.0150	Nil	1 : 5.4
-55°	1200	0.0045	0.0012	0.0037	Nil	1 : 2.9
-59°	1750	0.0110	0.0041	0.0130	Nil	1 : 3.1

solution of potassium permanganate to remove any impurity which would react with the ozone.

It was found that after a dilution of 1 part in one million it was no longer possible to detect the ozone. This is probably due to the destruction of the last traces by residual impurities in the diluent air. It is noteworthy to recall here the well-known fact that at a dilution of 1 part in 500,000 the gas possesses a decided odour, so that the smell constitutes one of the most delicate tests for this gas.

The results of the measurements made are given in Tables I. and II. The volume of the reagent used in the wash-bottle was in each case 5 cc. Since the cryoscopic point of potassium iodide solution is -24° , measurements below this temperature were made by leading the gas over the surface of the solid reagent. In these cases the reaction vessel was always joined in series with a second vessel containing liquid reagent through which the gas issuing from the first vessel was made to pass. It was found in every case that more than half of the ozone was removed by merely passing over the surface of the solidified reagent in the first vessel.

For the analysis of the liquid, 2 cc. were always withdrawn. In some cases a long interval was allowed to lapse before conducting the titration in order to see the

change on standing. The concentration of the ozone was calculated afterwards from the analyses of the reagent. There is some doubt whether the iodine liberated after using a neutral solution and then acidifying, is an exact measure of the amount of ozone (*cf.* Brunck, *loc. cit.*; also Ladenburg and Quasig, *Ber.*, 1901, [1], xxxiv., 1184), but in any case the approximation is sufficiently close for the present purposes.

The results of these measurements establish the following points:—

1. In the reaction between ozone and potassium iodide, the ratio of iodate (+periodate) to free iodine (+hypoiodite) increases with the total amount of ozone which is passed through the reagent, as has been pointed out by Garzarolli-Thurnlackh (*loc. cit.*).

The important result shown in the present work is that, through some operation of mass action, this ratio is also increased in a very marked manner with the concentration of ozone per unit volume even when the same total quantity of ozone is passed. At some point between 160 and 6 parts of ozone in one million of air no iodate is formed on further dilution, but only free iodine and hypoiodite.

However, at temperatures below -24° , when the reagent is completely solidified, this relationship no longer applies, as in these cases the smallest quantity of ozone gives more iodate than free iodine (+hypoiodite).

2. On allowing the reagent, which had been exposed to ozone to stand, a slow change took place, resulting in the cases of the more concentrated products, in a considerable increase in the quantity of free iodine, while any free alkali present gradually disappeared. This change is explained by reactions which have been found to take place between potassium iodide on the one hand, and peroxide and periodate (*cf.* Pechard and Brunck, *loc. cit.*).

When only small quantities of ozone have reacted, these changes with time are comparatively small, and need not be considered when the reagent is applied for approximate atmospheric measurements.

3. It is seen that the quantity of potassium hydrate formed is very much lower than the equivalent of iodine and hypoiodite present. With very dilute gas the amount of alkali liberated is too small to detect with phenolphthalein. It would appear from these results that very dilute ozone reacts with potassium iodide to give hypoiodite or some oxygen compound lower than iodate, and that this compound is in equilibrium with a small quantity of iodine.

It is apparent from this that the method of using potassium iodide and litmus-papers, whereby the hydrate formed colours the paper blue, is quite inapplicable for quantitative measurements.

B. Reaction between Potassium Iodide and Nitrogen Peroxide.

Oxides of nitrogen, for the purpose of these measurements, were prepared by acting on nitric acid with copper and admitting a small quantity of the gas generated to a gas-holder, together with a large excess of air, where it would become oxidised to the peroxide. Measured volumes of this gas were then drawn by means of an aspirator through the reagent contained in a small wash-bottle. The reagent was then analysed as in the earlier cases. It was found that after the addition of acid to decompose the iodate, the end-point in the titration with sodium thiosulphate was not very definite. Thus, after once removing the iodine from the acidified solution, a further quantity gradually appeared. This is caused by the nitrous acid—which remains after the reduction of the nitric acid or nitrogen peroxide—being again oxidised by the air. In this way it behaves as a catalyst leading to a gradual decomposition of the potassium iodide by atmospheric oxygen.

In the results of the measurements which are tabulated below, the quantity of iodine found in the successive

titrations after definite intervals of the acidified solutions are given.

The tables also show the ratio of iodate to free iodine formed directly when nitrogen peroxide reacts with neutral potassium iodide. These measurements could only be made with the highly diluted gas on account of the catalytic effect mentioned above with the more concentrated gas. As in the measurements with ozone, the reagent used in each case consisted of 5 cc. of equal weights of potassium iodide and water, 2 cc. were withdrawn for the analysis. After removal of the free iodine by sodium thiosulphate, 5 cc. of N/10 hydrochloric acid were added, and the liberated iodine again titrated.

Volume of gas (cc.)	Conc. of nitrogen peroxide (per cent.)	Free iodine, (mgrm. equiv. in total reagent)	Interval between successive titrations.	Combined I_2 (as KIO_3, KIO_4) mgrm. equiv. in total reagent.	Ratio combined iodine to free iodine.
A. Room Temperature.					
1000	0'0033	0'0004	5 hours	0'0011	1 : 2'75
			65 hours	0'00616	
3000	0'0024	0'00084	21 hours	0'0025	1 : 2'98
				0'0084	
6000	0'0017	0'0007	25 mins.	0'0038	1 : 5'4
				0'0063	
B. Temperature -50° .					
8000	0'0008	nil		0'0028	0 : 1
12000	0'00025	0'00028		0'00112	1 : 4

It is seen from these results that the presence of small quantities of oxides of nitrogen can be detected when accompanied by highly diluted ozone, since the former gas alone gives potassium iodate when reacting with iodide. Moreover the catalytic property of nitrogen peroxide in continuously liberating iodine from an acidified solution of potassium iodide provides a characteristic and very delicate test for this gas.

C. Reaction between Hydrogen Peroxide and Potassium Iodide.

The reactions brought about in this case have not been conclusively investigated hitherto, but it is known that on adding hydrogen peroxide to potassium iodide solution at first no visible reaction occurs, but afterwards a slight liberation of iodine results, followed by effervescence and evolution of oxygen.

In the present work measurements were made, in some cases by passing the vapour of hydrogen peroxide into potassium iodide solution, and in others by adding a solution of the former to the latter. Estimations of the reagent were then made for iodine, alkali, and iodate.

It was found that on gradually increasing the amount of hydrogen peroxide that the free iodine present (including hypoiodite) soon approached a limiting value. The relative quantity of free alkali formed was in all cases found to be much less than corresponded to the reaction $2KI + H_2O_2 = 2KOH + I_2$.

It was found that no trace of iodate (or periodate) was given in any case.

The conclusion derived from these analyses is that potassium hypoiodite is the main product of the reaction, and that this then reacts with more hydrogen peroxide according to the equation $KIO + H_2O_2 = KI + H_2O + O_2$. So that the main reaction, when a certain concentration is reached, consists in a catalytic decomposition of the hydrogen peroxide. In the case of very dilute gaseous mixtures the reaction of this compound is seen to be similar to that of ozone, thus preventing a distinction by means of potassium iodide.

However, a distinction between these two gases can always be made qualitatively by means of a solution of titanium sulphate in sulphuric acid. This solution becomes yellow in presence of very small quantities of hydrogen peroxide, but is unaffected by ozone.

Summary of Results.

The reactions of potassium iodide with ozone, hydrogen peroxide, and nitrogen peroxide show the following characteristics. With ozone the ratio of the different products is a function of the concentration of the gas and of the total amount passed. With a very dilute gas no iodate is formed, but only hypoiodite and free iodine, and no potassium hydrate.

However, at temperatures below -24° , the cryoscopic point of the reagent, this relation does not hold.

With nitrogen peroxide the reaction results mainly in the formation of iodate, whatever the dilution of the gas. In presence of an acid solution of potassium iodide, nitrogen peroxide even when present in minute quantities shows the property of continuously liberating iodine from the reagent when in presence of air. This reaction forms a distinguishing and very delicate test for this gas.

Hydrogen peroxide, at high dilutions, reacts with potassium iodide similarly to ozone. However, a definite distinction can be made between these gases by means of titanous acid.

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THE MECHANISM OF ANODIC REACTIONS
AND THE BEHAVIOUR OF IRON AND NICKEL
ANODES.*

By E. P. SCHOCH,
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NERNST's solution tension theory assumes essentially that metal particles separate from the mass of the metal and enter the liquid direct as ions. This notion was formed from the thermodynamic expression for the electrode potential, and as thermodynamic relations are entirely independent of the "paths" through which the transformations take place, we should not be surprised to find that a study of the details of the action leads us to assume an entirely different mechanism for the electrode changes, particularly in order to harmonise our conception with our present knowledge of the properties of electrons,

The existence of free electrons in metals makes it logical and permissible to assume that when a metal is in contact with an electrolyte, electrons enter the solution and neutralise the charges on the cations in the immediate vicinity. The difference of potential thus set up between the liquid and the metal draws the anions to the latter, and on contact they react with the metal right on the surface of the latter. The resulting compounds, if soluble, then enter the solution. Similarly, the action at a cathode, during electrolysis, consists of the projection of electrons into the electrolyte and the neutralisation by these electrons of cations near the cathode. The neutralisation takes place away from the cathode, and the separation of the neutral metals from the electrolyte and their deposition on the cathode is a subsequent change.

There are many facts that support the view that the neutralisation of cations takes place *within* the electrolyte; we need but recall the fact that the passage of the current is hindered but slightly by gas films such as are found on metals which exhibit the phenomenon of over-voltage, and that the passage of the current is hindered but slightly by films which cover the surface of the aluminium in the electrolytic rectifier when the aluminium acts as the cathode. Again, the neutralisation of the electric charges on cations while the latter are still within the liquid is indicated by the co-deposition of metals in the form of alloys, and by the observation of supersaturated neutral metal solutions in connection with their electrodeposition (*Zeit. Elektrochem.*, xiii., 1477; *Trans. Chem. Soc.*, 1907, 385; *Abh. Bunsen Ges.*, No. 3, p. 75). In the latter

instance, electric discharge does not necessarily take place "at a distance" from the cathode, but in the first-mentioned instance above, gas films certainly prevent direct contact between cations and cathode. That the passage of electrons from cathode to electrolyte through gas films actually takes place *readily* during electrolysis has been positively established by Guenther Schulze in his study of electrolytic rectifiers (*Ann. d. Phys.*, xxi., 929; xxii., 543; xxiii., 226; xxiv., 43; xxv., 775; xxvi., 372; xxviii., 787; and still later papers).

This modification of Nernst's original conception of cathode actions follows as a matter of course from our present knowledge of electrons and the immobility of positive electric charges. However, this does not compel any modification of Nernst's view applied to the anodic dissolution of metals; and it is probably on this account that the notion of the direct formation of cations from metals is still adhered to more or less definitely. Even Le Blanc (see Note), who was the first to point out that all electrode reactions take place with a finite velocity and hence involve chemical changes besides the electrical change, considered that "the usual conception of the primary formation of the metal ions" is able to account for this finite velocity if it is amplified by the idea that the *primary* cations undergo the chemical change of hydration before they are in their final form.

(NOTE.—M. Le Blanc, "Die Elektromotorischen Kräfte der Polarisation, und Ihre Messung mit Hilfe des Oszillographen," *Abh. Bunsen Ges.*, No. 3; see also Reichinstein, *Zeit. Elektrochem.*, 1910, xvi., 916, who observed polarisation even in those cases in which Le Blanc observed none definitely).

However, in this same publication Le Blanc states that the idea of a direct attack of the anions upon the metal anodes may also be assumed to be the course of the reaction, this chemical change determining the finite velocity. He states that at the time of the writing of that article (March, 1909) both mechanisms of anodic reaction must be admitted as equally possible, and he suggests that they may take place simultaneously, and that the conditions may make one or the other more prominent. However, he does not mention the direct "anion-metal" reaction beyond this general statement.

The notion of the direct formation of cations from metals has the vital defect of not taking into account, in any direct manner, the well-known specific effect of the particular anions present. For a striking illustration of the latter effect one need but point to the difference in the rate of the action of zinc with dilute sulphuric acid and with dilute hydrochloric acid; or to the marked effect of the small amounts of certain anions such as the chloration, added to sulphuric action in the Planté method of forming positive storage-cell plates. This specific effect of the anions is best accounted for by assuming a direct attack of the solid metal by the anion with the subsequent dissolution of the compound.

As the facts appear to the writer there is nothing in the behaviour of metal anodes that requires the assumption of the direct formation of cations from metals in contradistinction to the direct attack of the anode by the anions, and since the latter mechanism of the reaction must actually be assumed to take place in many cases, only this mechanism of the reaction will be considered in the remainder of the article.

This conception of anode changes takes care of the specific influence of the anions, and leads us to expect that the velocity of reaction depends upon *both* reacting components; but before the general behaviour of anodes can be considered some other facts must be taken into account.

Guenther Schulze (*Ann. d. Phys.*, xxviii., 789) has shown that in the electrolysis of phosphate, borate, &c., solutions with an aluminium anode, the following distinct layers are formed upon the metals:—First, a very thin, non-porous layer of oxide; second, a porous layer of oxide which becomes thicker with increasing potential,

* A Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, November 12, 1913.

and which is slowly but constantly reformed next to the metal as the layer next to the electrolyte is slowly dissolved; third, oxygen gas, which fills the pores of the porous film. He also observed an evolution of oxygen gas on the surface between the film and the electrolyte. His conclusions concerning the formation of these films are the following:—

1. The first, very thin, film of oxide on the metal is formed by the oxygen of the air.

2. This thin layer hinders or prevents direct access to the metal of complex anions such as sulphation, phosphation, &c., and under the stress of the potential drop through this layer, these anions dissociate, producing an equivalent number of oxygen ions which on account of their lesser bulk can pass through the oxide layer (and in passing through it perforate it) and then reach the metal surface to be discharged there. The oxygen discharged on aluminium naturally forms a new layer of aluminium oxide next to the metal, while the outer portion of this oxide layer, made porous by the passage of the oxygen ions, develops the porous layer.

3. As the oxide layer thickens, the potential fall in it becomes great enough for some of the ions to give up their electrons before they reach the electrode, thus forming oxygen gas: the passage of the free electrons through the dielectric is plainly shown by numerous fine sparks.

It is needless to follow Schulze's explanation beyond this point, because his other observations have no bearing on the question of ordinary anode actions. The following general conclusion may be drawn from his work and should be emphasised:—A film, or cover, over the surface of an anode will hinder or prevent the direct access to the surface of the metal of complex anions and will bring about the formation of oxygen ions from them. The latter pass on to be discharged on the surface of the metal.

This gives us all the facts necessary for the explanation of the chemical change of any anode in any electrolyte. Briefly this explanation may be stated as follows:—With a clean anode surface the anions come in direct contact with the metal, react with it, and give up their electrons: the rapidity of the reaction and the final products obtained will vary greatly with different metals and different anions. The product may be so rapidly formed and so rapidly dissolved that other anions may have unhindered access to the surface. Again, the reaction may take place slowly, or the product may dissolve slowly, or the latter may be insoluble, or it may be hydrolysed into an insoluble compound, so that other ions may find their progress to the anode more or less obstructed—a condition that may naturally be brought about in almost any case by a sufficiently great current density. Many complex ions which are prevented by the obstruction from reaching the surface of the metal will dissociate into an equivalent number of oxygen ions, which reach the surface of the metal more readily. Upon discharge these oxygen ions may form the oxide of a metal (as with copper in sulphate electrolytes), or they may form partly an oxide and partly oxygen (as with platinum in sulphate electrolytes), or they may react so slowly that the discharged oxygen still in contact with the metal becomes gradually more condensed as more oxygen ions are forced into the same area with a greater potential difference until finally gaseous oxygen, or perhaps some higher oxide of the metal, is formed.

(To be continued).

Iron and Steel Institute.—The Annual Meeting will be held, by kind permission, at the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, May 7 and 8, 1914. The Bessemer Gold Medal will be awarded to Mr. Edward Riley, F.C.S. The Annual Dinner will be held in the Connaught Rooms, Great Queen Street, W.C., on Thursday, May 7, 1914. The Autumn Meeting will be held at Paris, on September 18 to 23, 1914, by the kind invitation of the Comité des Forges de France.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

THE ROLE OF FLUORINE IN ANIMALS.

For more than a century past the existence of fluorine had been known in the teeth and bones. Taking up these researches with M. Clausmann, M. Armand Gautier established in 1912 that fluorine is spread through all the organs of animals, but in very different proportions. There are 190 mgrms. in the enamel of the teeth and 0.750 mgrm. in the muscles. What is the role of this very active substance? MM. Gautier and Clausmann have established the fact that fluorine accompanies phosphorus everywhere, without however being proportional to it. Analyses made of the white and yellow of egg, of different milks, of the blood of carnivorous animals and herbivorous animals show that fluorine and phosphorus increase and decrease together. In the noble tissues of intense life, the brain, liver, pancreas, it is found that one part of fluorine suffices to bind 450 to 750 parts of phosphorus. In the hard tissues of life—bones, cartilages—one part of fluorine binds on an average only 150 times its weight of phosphorus. In the tissues of products of excretion, products of mechanical defence, or of ornamentation, such as hair, nails, feathers, epidermis, the fluorine no longer retains more than 3.5 or seven parts of phosphorus. Henceforth having become unfit for life, the fluorine is thrown off by the fall of the hair, down, or epidermis. Thus the accumulation of fluorine in these products, which in themselves are not inherent to life and are destined to be thrown out.

A GIGANTIC ELECTRO-MAGNET.

For some time past physicists have been seeking to realise extremely powerful electro magnets so as to be able to examine the intimate construction of matter. Already Prof. Jean Becquerel had succeeded in having an electro-magnet constructed of a magnetic power of 50,000 gauss. This apparatus, weighing more than 1100 kilograms., lately installed in the cellars of his laboratory, has not yet been experimented with. Recently the Academy of Sciences had a very interesting communication from M. Deslandres, the learned director of the Observatory of Meudon, who, in his own name and in that of Prof. Perot, has shown two models of electro-magnets enabling powerful fields to be obtained with apparatus of low weight. The different pieces of the unmounted electro-magnet very much interested the members of the Institute. The apparatus does not weigh more than 30 kilograms., and at its full force, 50,000 gauss was reached and even exceeded. The characteristic of these electro-magnets is the employment, as conductors, of thin copper bands, furnished with a system for cooling with petroleum, carried to 30° below zero. It is well known how much interest is attached to these researches on account of the importance of magnetic effects on the emission and absorption of light. In astronomy the study of emitted light has enabled important magnetic fields to be recognised on the surface of the sun. M. Appel, president of the learned assembly, commented on this interesting communication, and suggested the idea of the construction of a much more powerful electro-magnet, destined to be used in the Sorbonne and in a cold laboratory for the study of very low temperatures analogous to the laboratory of Prof. Kamerlingh Onnes at Leyden. This double erection would contribute to found a centre of scientific studies that does not at present exist in Paris.

THE INSTALLATION OF PROF. CHARLES RICHEL.

Prof. Charles Richet, elected a week ago titular member of the Academy of Sciences in the section of medicine and surgery, was present at this week's sitting of the Academy. The President, M. Paul Appel, Dean of the Faculty of Science, at the opening of the meeting, welcomed the eminent physiologist, and invited him to take his place among his colleagues.

EULOGY OF SIR DAVID GILL.

M. Appel mentions the death of the learned English astronomer, Sir David Gill, correspondent of the French Academy of Sciences since 1896, and a great friend of France.

A NOTICE ON M. RADAN.

According to academical tradition, which requires that each newly elected member shall make the historical praise of his predecessor and which is now adopted by the Academy of Sciences, M. Pierre Puiseux, astronomer of the Paris Observatory, reads a paper on the life and works of M. Radan, eminent astronomer and delicate writer, who died a little over two years ago, and who is succeeded by M. Puiseux.

CURIOUS ANALOGIES BETWEEN INSECTS AND CRUSTACEÆ.

Insects and crustaceæ being animals belonging to two different classes have, generally, organs that are very differently constituted. In a study presented by M. Henneguy, M. Lecaillon, Professor at the Faculty of Science of Toulouse, shows that certain insects, the collembolæ, have nevertheless an ovary, the construction of which resembles that of the ovary of a little crustacean, the chirocephalopod. The fact is interesting from a biological point of view, and particularly from a phylogenical point of view.

A MERCURY ARC WITH ALTERNATE CURRENT.

Two young physicists, M. Maurice Leblanc, jun., and M. Darmon, have just, for the first time, succeeded in realising a mercury arc with alternate current. In their work, communicated by Prof. Boity, they mention that with this arc, for a luminous intensity of 3000 candles, the consumption does not exceed 0.21 watt per candle. It is also possible to prime or light an arc even when there is an empty space between the electrodes.

THE INFLUENCE OF TEMPERATURE ON ASTRONOMICAL OBSERVATIONS.

In astronomy many measures of precision are taken by means of micrometric screws, worked up with the greatest care, so that all the threads are exactly equal, but the angular value of the thread is modified by the variations of temperature. The determination of this influence of the temperature is a long and delicate operation. M. Bigourdan has indicated a simple process to arrive at this result, by utilising a method recently explained by M. Lippmann, so as to obtain the veritable focal distance of an objective by autocollimation.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, January 29th, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Origin of Thermal Ionisation from Carbon." By Prof. O. W. RICHARDSON, F.R.S.

In a paper recently communicated to the Society by Dr. J. N. Pring, experiments bearing on this subject were described. The smallness of the observed currents and the variation of them with the pressure and nature of the gas, led Dr. Pring to the conclusion that considerable doubt was thereby cast on the theory of the emission of electrons from hot solids, and that these effects were to be attributed to chemical action.

In the present paper the magnetic field due to the large heating currents employed by Dr. Pring are shown to curl up the paths of the electrons, and so prevent them from reaching the electrode. It is shown that with the larger

currents none of the electrons could reach the electrode in these experiments, and owing to the complexity of the apparatus it is impossible to say what proportion would reach it at the lower temperatures.

It is pointed out that an increase of the observed currents is to be expected on account of—(a) the interference of the gas molecules with the motion of the electrons, and (b) the combination of electrons with atoms and molecules of the gases.

In the opinion of the author of this paper, the conclusions referred to cannot be regarded as established by the experiments under consideration.

"The X-ray Spectra given by Crystals of Sulphur and Quartz." By Prof. W. H. BRAGG, F.R.S.

A crystal of quartz is found, on examination by the X-ray spectrometer, to contain three interpenetrating hexagonal lattices of silicon atoms and six of oxygen. The angles of reflection in a number of important planes all agree, within 1 or 2 per cent, with the calculated values. Sulphur contains eight interpenetrating lattices, each of the kind formed by placing an atom at each corner of a rectangular parallelepiped and in the centres of two opposite faces. The edges of the parallelepiped are in the known ratios of the crystallographic axes. One element of the movement by which the eight lattices can be successively derived from each other consists of a translation along the "c" axis equal to one-eighth of the length of that axis.

"Temperature Variation of the Photo-elastic Effect in Strained Glass." By Prof. L. N. G. FILON, F.R.S.

The experiments described in this paper were undertaken to see whether the double refraction produced in glass by stress was at all affected by change of temperature.

The apparatus in which the specimens were strained under flexure was enclosed in a copper box with hollow walls, in which steam could be made to circulate freely. The refractive indices were then measured by a method described in *Roy. Soc. Proc.*, A, lxxiii., 572–579.

The glasses examined were Jena "Uviol" glasses, examined at ordinary temperatures some years previously. These were heated to 90°, and photographic observations of the refractive indices taken. After cooling again to 18° the observations were repeated.

The results show that the refractive indices for rays polarised in and perpendicular to the line of stress are unequally affected, but seem increased on the whole by rise of temperature.

One of these, however, shows a permanent residual change even after cooling. This is important as showing that this property of the glass is affected by previous temperature treatment.

Various irregularities in the graphs of the refractive indices are also discussed.

"Studies in Brownian Movement. Paper I. Brownian Movement of the Spores of Bacteria." By J. H. SHAXBY and E. EMRYS ROBERTS, M.D.

"Transmission of Cathode Rays Through Matter." By R. WHIDDINGTON, D.Sc.

"Variation with Temperature of the Specific Heat of Sodium in the Solid and the Liquid State; also a Determination of its Latent Heat of Fusion." By EZER GRIFFITHS.

The specific heat of sodium (melting-point 97.6°) was investigated at various temperatures in the range 0° to 140° by the electrical method. The range of temperature through which the metal was heated was about 1.5°, thus enabling the actual specific heat at each particular temperature to be determined.

In the solid state the specific heat is considerably influenced by the nature of the previous heat treatment, and two distinct specific heat temperature curves are obtained for the annealed and the quenched state.

The increase in the values of the specific heat in the solid state is very marked as the melting-point is ap-

proached. The variation may be indicated by the following approximate values of the atomic heat for the annealed state :—

Temperature ..	0°	50°	96°
Atomic heat ..	6.5	6.8	7.5

In the molten state the specific heat decreases with temperature, the relation between specific heat and temperature from 100° to 140° being linear. The latent heat of fusion was found to be 27.52 grm. calories.

"Natural Radiation from a Gas." By GEORGE GREEN, D.Sc.

The investigations of Planck have established the result that the total energy emitted from a black body at any temperature consists of discrete quanta, all equal and similar. This does not necessarily imply that energy has an atomic structure. It may arise from the nature of the radiating molecules, which may be such that emission of energy takes place accompanied by some definite change within the molecule, such as the expulsion of an electron or the rearrangement of the system in a new equilibrium condition. If we identify the "energy quantum" as the energy contained in the light pulse emitted each time a molecule undergoes some such structural change, the determination of the form of this light pulse might lead to useful information regarding the constitution of the molecule.

In this paper the form of pulse, in which the energy per wave-length is the same as that required by Planck's Law of Radiation at any temperature, is first derived. This form accordingly represents the total radiation from any black body at any temperature. The radiating body is now taken to be a gas. By decomposing the above pulse we obtain an infinite succession of wave-trains emitted by the various groups of molecules obtained by arranging the total number according to speed.

"Similarity of Motion in Relation to the Surface Friction of Fluids." By Dr. T. E. STANTON and J. R. PANNELL.

The paper deals with an experimental investigation of the existence of the similarity of motion in fluids, of widely differing viscosities and densities, in motion relative to geometrically similar surfaces, which has been predicted from considerations of dynamical similarity by Stokes, Helmholtz, Osborne Reynolds, and Lord Rayleigh. The theory in its most general form may be expressed by the relation—

$$R = \rho v^2 l \left(\frac{v \cdot L}{\nu} \right)$$

where R is the resistance per unit area of the surface, ρ density of the fluid, v velocity, L a linear dimension of the surface, ν kinematical coefficient of viscosity of the fluid, and the assumptions made in the derivation of the expression are that R depends solely on ρ , L , v , and ν .

The method of experimentally demonstrating the sufficiency of these assumptions has been by a determination of the surface friction of air and water flowing through smooth pipes of varying diameters and with as great ranges in velocity as possible, and so obtaining values of the condition for similarity of motion, which is that for the same values of $v \cdot d / \nu$ in either fluid the values of $R / \rho v^2$ should be identical.

The experiments show that this condition is fulfilled with considerable accuracy through a range in the value of $v \cdot d / \nu$ of from 2500 to 430,000. To obtain this range with the comparatively small diameters of pipes used, mean velocities of flow up to 6000 centimetres per second have been reached.

From these data it has been possible to investigate the limits of accuracy of the well-known Index Law of the Resistance of Fluids, $R = k v^n$, and by a determination of the value of n at different points of the range of velocity it appears that n is not constant for any particular surface but gradually increases as the value of $v \cdot d / \nu$ increases. In this way gradual variations in the value of n from 1.72 to 1.92 have been detected.

"Influence of Molecular Constitution and Temperature on Magnetic Susceptibility." By A. E. OXLEY.

"Boiling-point of Sulphur on the Thermodynamic Scale." By N. EUMORFOPOULOS.

CHEMICAL SOCIETY.

Ordinary Meeting, January 22, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

THE PRESIDENT referred to the loss sustained by the Society, through death, of William Popplewell Bloxam and John Gibson.

It was announced that the Council desired to draw the attention of Fellows to the fact that the Faraday Society is prepared to consider the election to membership of a certain number of Fellows of the Chemical Society without the usual entrance fee.

Certificates were read for the first time in favour of Messrs. Sydney Edward Davenport, Fernbank, York Road, Windsor; Charles George Fernie, B.Sc., Holmleigh, Northwood, Middlesex; George Ingle Finch, 41, Ladbroke Road, W.; Reginald Furness, M.Sc., 90, Woodlands Road, Ansdell, Lytham; Gopal Balkrishn Kolhatker, M.A., Ferguson College, Poona, India; Frederic William Leighton, Lydiard Tregoze, Wootton Bassett, Swindon; Rowland Ernest Oldroyd, 90, Park Road, Rochdale; William Henry Pick, B.Sc., 141, Mare Street, Hackney, N.E.; Frederick Alfred Pickworth, 70, Highfield Road, Dartford; Conly Hunter Riley, Anchorage, Clayton-le-Moors, Accrington; Joseph de Carle Smith, B.Sc., Oak House, Newmarket Road, Norwich; Horace Gilbert Stone, B.Sc., 24, High Street, High Wycombe.

A certificate has been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Mr. Lionel Cohen, Stock Department Laboratory, Casino, N.S.W.

Of the following papers, those marked * were read :—

*1. "Crystals of Organic Compounds Coloured Blue by Iodine." By GEORGE BARGER and WALTER WILLIAM STARLING.

In a previous paper (Barger and Field, *Trans.*, 1912, ci., 1396) it was pointed out that the blue compounds formed from various organic substances and iodine may be either amorphous or crystalline; the former cases are typical examples of adsorption. The blue crystals may be regarded as solid solutions of iodine in the organic substance, in proportions not necessarily stoichiometric. They only result when the crystal is formed in the presence of iodine, either from a solution containing iodine, or by sublimation in the presence of iodine (compare for analogous cases Bruni, "Feste Lösungen und Isomorphismus," 1908, p. 95). Colourless crystals of the organic substance, when once formed, cannot be made to take up iodine. In most of the cases studied so far, the blue crystals have been obtained from solutions in mixtures of water with an organic solvent, but this need not be the case always; narceine, for instance, when dissolved, together with iodine, in pyridine, gives rise to blue crystals on adding light petroleum. All the blue crystals examined so far are more or less strongly pleochroic; no connection has been detected between the crystalline form and the capacity for yielding "mixed" crystals with iodine.

DISCUSSION.

In reply to the President, Dr. BARGER expressed the opinion that the additive compounds described might be analogous to oxonium compounds, but since they were also given by substances not containing a pyrone nucleus, they might possibly show greater analogy to the potassium additive compounds of ketones, described by Schlenk and Thal (*Ber.*, 1913, xlii., 2840). No analogous bromine compounds had been observed.

*2. "The Mutual Solubility of Formic Acid and Benzene, and the System: Benzene-Formic Acid-Water." By ARTHUR JAMES EWINS.

Formic acid was found to be partly miscible with a number of organic liquids. The mutual solubility of formic acid with benzene was studied in detail.

The critical solution temperature (maximal) of these two liquids affords a very sensitive means of determining the purity of the components, and was therefore employed for this purpose. For the purification of formic acid, fractional distillation was employed, followed by careful fractional crystallisation, until the critical solution temperature with pure benzene remained constant (73.2°).

The acid so obtained melted at 8.39° , boiled at $100.47^\circ/760$ mm., and had $D_{20}^{25} 1.2259$. The acid showed very little supercooling on freezing, the actual figures in three determinations being 0.40° , 0.15° , and 0.35° .

Benzene was purified by fractional crystallisation and distillation from sodium. The melting-point was found to be 5.57° . The ternary system benzene-formic acid-water was also studied.

*3. "The Condensation of Ethyl Glutaconate." By RAYMOND CURTIS and JAMES KENNER.

The condensation products isolated by Blaise (*Comptes Rendus*, 1903, cxxxvi., 639) and by von Pechmann (*Ber.*, 1904, xxxviii., 2113) from the action of sodium ethoxide on glutaconic ester were shown to be identical, and a probable constitution was assigned to them. Certain discrepancies between the accounts given by the two investigators named were also examined.

α -Ethylglutaconic ester, after treatment with sodium ethoxide in the same manner as glutaconic ester, was recovered unchanged.

DISCUSSION.

Prof. J. F. THORPE stated that his experience with the behaviour of ethyl glutaconate on alkylation led him to think that the action of ethylene dibromide on this substance would most likely yield a derivative of cyclopentane, and not the cyclopropane derivative suggested by Dr. Kenner. It would be of great interest to apply this reaction to the case of ethyl β -methylglutaconate, the two forms of which were sufficiently stable to withstand ordinary experimental conditions.

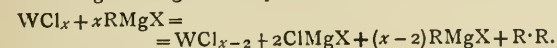
Dr. KENNER, in reply, pointed out that Fecht had proved one of the products of the condensation of ethyl glutaconate with ethylene dibromide to be a cyclopropane derivative by the identity of its reduction products with a synthetic acid of known constitution.

*4. "2 Hydrindamine." By JAMES KENNER and ANNIE MOORE MATHEWS.

The preparation of 2-hydrindamine from ethyl hydrindene-2-carboxylate by Curtius's method was described, and the base was characterised by means of a number of derivatives.

*5. "An Attempt to Prepare Organometallic Derivatives of Tungsten." By EUSTACE EBENEZER TURNER.

It was shown that tungsten, in common with all elements situated in even series or in sub-group A of the periodic classification, cannot be converted into organometallic compounds by means of the Grignard reagent. The higher chlorides of tungsten are, instead, reduced, the chlorine removed decomposing the Grignard reagent to produce a mixed magnesium haloid salt and a hydrocarbon consisting of the two diaryl residues linked together, according to the general equation—



*6. "The Absorption Spectra of Nitrated Phenylhydrazones." By JOHN THEODORE HEWITT, RHODA MARIANNE JOHNSON, and FRANK GEORGE POPE.

The absorption spectra of the β -nitrophenylhydrazones of benzaldehyde and acetophenone have been measured. Addition of alkali to the alcoholic solutions leads to salt-formation, accompanied by considerable change in the

absorption spectra. The absorption of the two hydrazones mentioned is very similar to that of β -nitrobenzaldehyde-phenylhydrazone, although when the latter compound is acetylated, the absorption experiences a strong displacement towards the ultra-violet.

*7. "Unstable Compounds of Cholesterol with Barium Methoxide." By EDGAR NEWBERRY.

Barium oxide in presence of excess of methyl alcohol forms an unstable solid compound with cholesterol, which is dissociated in organic solvents, such as ether, benzene, &c., to an extent depending on the temperature and also on the concentration of the excess of methyl alcohol present, a state of equilibrium being set up between the cholesterol in the solid and that in the liquid. This state of equilibrium is attained much more rapidly when the compound is being decomposed than when it is forming. The compound is readily decomposed by water, carbon dioxide, or acetic acid. Hexadecyl alcohol shows a similar behaviour to cholesterol.

A knowledge of the above reactions is of importance when attempting to extract cholesterol and cerebroses by Smith and Mair's method (*Journ. Path. Bact.*, 1910, xv., 122).

*8. "A Study of the Vapour Pressure of Nitrogen Peroxide." By ALFRED CHARLES GLYN EGERTON.

Following some work on the vapour pressure of bromine, and in connection with the measurement of small quantities of nitrogen peroxide, the vapour pressure of solid nitrogen peroxide has been investigated down to as low a temperature as -100° . The method employed in these measurements consisted in the saturation of a known volume of hydrogen, as it passed over the nitrogen peroxide, and the estimation of the amount of the latter carried over.

The measurements follow a certain curve which has a somewhat steeper slope than other measurements would appear to indicate, although these have not, so far, been carried below -35° . The vapour pressure curve of nitrogen peroxide was discussed, and, with the aid of Nernst's vapour pressure equation, approximate values of some of its chemical and physical constants were derived.

*9. "Organic Derivatives of Silicon. Part XXI. The so-called Siliconic Acids." By ARTHUR JAMES MEADS and FREDERIC STANLEY KIPPING.

Many compounds supposed to have the structure $R \cdot Si \cdot OH$ and to represent the silicon analogues of the carboxylic acids have been described in the literature. The first case was that of silicopropionic acid, $EtSiO_2H$ (Friedel and Ladenburg); shortly afterwards silicoacetic acid, $Me \cdot SiO_2H$, silicobenzoic acid, $Ph \cdot SiO_2H$, and silicotoluic acid, $C_6H_4Me \cdot SiO_2H$, were described by Ladenburg (*Ann.*, 1875, clxxix., 143). In more recent times many other aliphatic and aromatic siliconic acids have been prepared by Khotinsky and Seregenkoff (*Ber.*, 1908, xli., 2946), and by Melzer (*Ber.*, 1908, xli., 3390).

Now the results of the study of the diarylsilicanediols, $R_2Si(OH)_2$ (Kipping, *Trans.*, 1912, ci., 2108, 2125; Robison and Kipping, *Ibid.*, 2142, 2156), seemed to indicate that compounds of the type $RSi(OH)_3$ would not pass into siliconic acids, $R \cdot SiO_2H$, by loss of the elements of water, but would give rise to a series of condensation products, probably analogous to those of the diarylsilicanediols. An exhaustive examination of the so-called silicobenzoic acid has gone far to establish this view; the product of the hydrolysis of phenylsilicon trichloride is not one compound of the composition $C_6H_5 \cdot SiO_2H$, but a complex mixture of condensation products, primarily derived from the trihydroxy-derivative, $C_6H_5 \cdot Si(OH)_3$. It is very probable, therefore, that all the so-called siliconic acids are merely mixtures; the experiments are being continued in order to test this inference.

*10. "The Reactions of isoAmarine." By HENRY LLOYD SNAPE.

isoAmarine and methyl iodide react at the ordinary tem-

perature, when benzene is employed as a solvent, with the production of the *methiodide*, $(C_{21}H_{18}N_2)_2 \cdot CH_3I$, which, on crystallisation from benzene, melts at 135° .

By the action of acetyl chloride on a solution of *isoamarine* in ethyl acetate or chloroform and heating the product with absolute alcohol, a crystalline substance, melting at $235-236^\circ$, was obtained, which proved to be an isomeride of the compound called "*diacetylamarine*" by Bahrmann, but shown by Japp and Moir (*Trans.*, 1900, lxxvii., 636) to be acetylbenzoyldiphenylethylenediamine, $C_{23}N_{22}O_2$, which melts at 316° . The six-sided plates mentioned in a former paper (*Trans.*, 1900, lxxvii., 780) as having been obtained in small quantity as the result of the action of acetyl chloride on *isoamarine* followed by treatment with alcohol, proved to be *isoamarine hydrochloride*.

When *isoamarine*, dissolved in a very small quantity of glacial acetic acid, was treated with fuming nitric acid, a *mononitro*-derivative was obtained, which melted at $82-85^\circ$. Fuming nitric acid at 60° acted on *isoamarine*, forming a *dinitro* derivative, which melted at $175-176^\circ$.

The values previously published for the rotation of *d*- and *l*-*isoamarine* and of the corresponding tartrates have been corrected.

Sulphates of *d*- and *l*-*isoamarine* were described. The former has the formula $(C_{21}H_{18}N_2)_2 \cdot H_2SO_4$, melts at $266-267^\circ$, and its rotatory power, $[\alpha]_D^{25}$, is $+151.1^\circ$ to $+155.7^\circ$. The corresponding particulars with respect to the *l*-*iso*-salt are $(C_{21}H_{18}N_2)_2 \cdot H_2SO_4 \cdot \frac{1}{2}H_2O$, $280-285^\circ$, and -144.1° . On addition of nitrosyl sulphate to *d*-*isoamarine* sulphate, a white crystalline substance is precipitated which has the composition $(C_{21}H_{18}N_2)_2 \cdot H(NO)SO_4 \cdot \frac{1}{2}H_2O$.

11. "*The Constituents of Solanum angustifolium: Isolation of a New Gluco-alkaloid, Solangustine.*" By FRANK TUTIN and HUBERT WILLIAM BENTLEY CLEWER.

The material employed in this investigation consisted of the leaves, twigs, and flowers of *Solanum angustifolium*, Ruiz et Pavon.

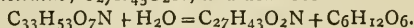
For the purpose of a complete examination, 30.92 kilograms of the dried and ground material were completely extracted with hot alcohol, and the resulting extract distilled with steam.

From the portion of the extract which was soluble in water, there were isolated the following substances:—(i.) Quercetin; (ii.) rutin; (iii.) *l*-asparagine; (iv.) a new gluco-alkaloid, *solangustine*, $C_{33}H_{53}O_7N \cdot H_2O$. The aqueous liquid also contained small amounts of an amorphous alkaloid and a considerable quantity of sugar, together with amorphous viscous products which, on hydrolysis, yielded quercetin and 3:4-dihydroxycinnamic acid.

The portion of the extract which was insoluble in water yielded the following definite substances:—(i.) Triacotane; (ii.) a phytosterol, $C_{27}H_{46}O$; (iii.) a phytosterolin (phytosterol glucoside), $C_{33}H_{56}O_6$; (iv.) palmitic, stearic, cluynitic, and cerotic acids, together with a mixture of linolic and linolenic acids.

The *hydrochloride*, *nitrate*, and *sulphate* of *solangustine* are insoluble in water and most organic solvents. The last mentioned salt forms colourless needles, and has the formula $(C_{33}H_{53}O_7N)_2 \cdot H_2SO_4 \cdot 3H_2O$.

On hydrolysis with dilute acid, *solangustine* yields *solangustidine*, $C_{27}H_{43}O_2N$, and dextrose—



Solangustidine is amorphous, but a crystalline *hydrochloride*, *hydrobromide*, *nitrate*, *sulphate*, *picrate*, and *acetyl* derivatives have been prepared from it.

The entire alcoholic extract of the plant, the new gluco-alkaloid, *solangustine*, and the amorphous, alkaloidal material were separately administered to a dog, but produced no appreciable physiological effect.

12. "*Studies of the Constitution of Soap Solutions: Electrical Conductivity of Potassium Salts of Fatty Acids.*" By HUGH MILLS BUNBURY and HERBERT ERNEST MARTIN.

The conductivities of the potassium salts (soft soaps) of the saturated fatty acids of even number of carbon atoms from the stearate to the acetate have been measured at 90° by the somewhat laborious method previously described by McBain and Taylor.

The conductivities of the potassium soaps are higher than those of the corresponding sodium soaps, but there is a general resemblance between the form and position of corresponding curves. Closer comparison shows an even greater tendency towards abnormality on the part of the potassium salts; this is not due to the potassium ion as such, for well-developed maxima and minima in the conductivity curves are exhibited from the stearate as far down as the laurate (C_{12}).

The appearance, washing power, density, and conductivity curve of potassium hexoate (C_6) distinctly mark the beginning of that deviation from the behaviour of the acetate, which rapidly and regularly increases through the other members of the homologous series until it attains the typical character of the higher soaps.

In all cases where it is directly visible, the depression in the conductivity curve occurs in the same region of concentration, independent of the nature of the acid or alkali taken. Further investigation may, however, show that the real abnormality is shifted in the case of the lowest homologues to regions of higher concentration.

13. "*The System: Ethyl Ether—Water—Potassium Iodide—Mercuric Iodide. Part I. The Underlying Three-component Systems.*" By ALFRED CHARLES DUNNINGHAM.

The System: Potassium Iodide—Mercuric Iodide—Water.—This system has been studied at 20° and 30° . In both cases the following phases are stable in equilibrium with solution:—KI, $KHgI_3$, $KHgI_3 \cdot H_2O$, HgI_2 .

The System: Potassium Iodide—Water—Ethyl Ether.—Ether and water are only miscible to a small extent, and this is not materially increased by the addition of potassium iodide. Consequently it is possible to obtain:—(1) A small range of homogeneous aqueous solutions in equilibrium with potassium iodide, (2) a small range of homogeneous ethereal solutions in equilibrium with potassium iodide, (3) one pair of invariant aqueous and ethereal solutions in equilibrium with one another and with potassium iodide, and (4) a wide range of conjugate aqueous and ethereal solutions in equilibrium with one another.

The System: Potassium Iodide—Mercuric Iodide—Ethyl Ether.—The following phases are stable in equilibrium with solution:—KI— $KHgI_3$ — HgI_2 . Under certain conditions a heavy liquid layer separates, rich in dissolved salts, and an equilibrium diagram has been constructed in which the saturation curves of potassium mercuri-iodide and mercuric iodide are cut by a binodal curve, so that each is divided into two portions, separated by a region in which all mixtures exist as two liquid layers.

The System: Mercuric Iodide—Water—Ethyl Ether.—Mercuric iodide is almost insoluble in water and ether, and all mixtures of these two components. The equilibrium is of the same type as that in the system: potassium iodide—water—ethyl ether.

14. "*The Inversion of Sucrose by Acids in Water-alcohol Solutions.*" By GEORGE JOSEPH BURROWS.

The rate of inversion of sucrose by acids in water-ethyl alcohol mixtures decreases with increasing concentration of alcohol up to 45 to 50 per cent, and then increases. The catalysis in such a series of solvents is therefore not proportional merely to the concentration of hydrogen ions. The catalytic activity of an acid is affected by the viscosity of the solution, and the influence of the latter is probably the same as in conductivity. If therefore the rates of inversion are divided by the conductivities of the acid in the different solvents, the numbers so obtained represent the relative catalytic activities of the acid. In this way it was found that the replacement of water by alcohol increases the catalytic activity of hydrochloric acid.

In the inversion of sucrose by acids, therefore, the

addition of water may be regarded as decreasing the catalytic activity of the hydrogen ions. This agrees with results obtained by other authors for the anti-catalytic effect of the addition of water in esterification and similar catalytic reactions in alcohol.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, January 23rd, 1914.

Prof. C. H. LEES, F.R.S., Vice-President, in the Chair.

A PAPER entitled "*Some Characteristic Curves and Sensitiveness Tests of Crystal and Other Detectors*," was read by Mr. P. R. COURSEY.

The paper describes some experiments recently conducted on different types of wireless detectors, which were undertaken with a view to finding out whether any definite relation could be traced between the sensitiveness and characteristic (or, volt ampere) curves of a detector.

Sample curves for some of the most common detectors are included in the paper and show that in some cases a fairly good agreement exists between the sensitiveness curve of a detector and the second differential of its characteristic, this being most notably the case in the more stable of the crystal detectors, but at the same time it is abundantly evident that the flexure of the characteristic curve cannot be the only cause of the response of a detector to wireless signals, but that at least a second action must also be present, as in some cases—notably the electrolytic detector—it was observed that the maximum ordinates on the second differential, *i.e.*, the point of greatest change of flexure of the characteristic curve, were at places where the measured sensitiveness was either zero or extremely small, showing that there are probably at least two actions opposing one another at this point. As this is most prominent in the case of the electrolytic detector, it perhaps suggests that this additional action when present in other detectors is electrolytic in nature, or that the received oscillations when superimposed on the direct-current boosting voltage partake of the properties of some "trigger" action (such as in the Zehnder trigger cymoscope). This view is supported by experiments with detectors of the tellurium-aluminium type.

DISCUSSION.

Prof. J. A. FLEMING thought it was impossible to avoid speculation in connection with these interesting effects. He thought the real cause of the asymmetry in the case of valve-detectors was the emission of electrons from the hot filament. The laws governing this emission had been shown to be analogous to those governing the evaporation of water. Consequently it could be increased by applying a negative pressure. Some of the irregularities observed might be the equivalent phenomenon to boiling with bumping. He thought it would be of interest if Mr. Coursey's experiments could be repeated at different temperatures.

Mr. W. DUDELL thought the investigation was extremely difficult, as one could not be certain that a given pair of crystals would always work in the same way. As far as the crystal detectors were concerned, he did not think the relation between the sensitiveness and the second differential of the characteristic curve was very clear. The determination of the second differential curve was very difficult unless the original observations could be reproduced very accurately.

Dr. W. ECCLES thought that the agreement between the characteristic curves given in the paper and those given for the same pairs of substances by previous experimenters showed that the shapes of the curves were undoubtedly dependent on the physical properties of the substances more than on the configuration of the contact. A theory of the cause of the shape of the characteristic curve had been published. The present paper dealt, however, with

quite a different matter, namely, the connection between the shape of the curve and the sensitiveness of the detector; the theory of this was also known and was chiefly a matter of geometry.

Mr. D. OWEN asked what the measure of sensitiveness adopted by the author was; also if he could furnish figures as to the actual voltage across the contact at limiting silence in the telephone. He would suggest that prediction of the sensitiveness of a particular individual detector might be more simply made from inspection of an alternating voltage characteristic—that was, from a graph in which the direct current through the contact under an alternating low-frequency voltage was plotted as ordinate against the alternating volts as abscissa.

Dr. R. S. WILLOWS thought the characteristic curve given for the oscillation valve was not a good one for the purpose. If lower voltages had been used the curve would have possessed three distinct branches. In his experience of the valve, the detector was most sensitive when the voltage was boosted up until it was just at the point of producing ionisation by collision. By making use of the electronic emission from hot lime a better cathode was obtained than in the case of the carbon filament.

Prof. G. W. O. HOWE thought too much weight had been attached to slight changes in the characteristics of the crystal detectors. A minute alteration in the point of contact greatly altered the properties of the detector. It would be interesting to hear if Mr. Coursey had repeated his observations. Sometimes a polarising voltage greatly improved the sensitiveness while the slightest shifting of the point might render the polarising voltage quite useless. Since they were so sensitive to slight changes in the conditions, much stress should not be laid on little variations in the characteristic.

Mr. E. H. RAYNER thought that some of the irregularities in the characteristics might easily be due to vibration and similar disturbances. He thought it would be useful if the author gave some idea of the resistance of the detectors at maximum sensitiveness, so that one could see if the telephone was doing justice to the detector.

Prof. FORTESCUE had also found crystal detectors very sensitive to disturbances, such, for example, as the passing of a motor 'bus near the laboratory, and he thought that slight changes from one characteristic to another, rather than real changes in the characteristic, would account for some of the irregularities shown.

The AUTHOR, in reply, agreed with Dr. Fleming that it would probably be of great value to conduct experiments similar to those described in the paper at various temperatures, both above and below the ordinary, as in this manner a better insight might be obtained, from the experimental point of view, as to the part played by thermal effects at the contact of the two crystals. The fact that it was unnecessary to have at least one of the contacts of low thermal conductivity was supported by the tests on the tellurium-aluminium detector, in which both materials were metals. These tests seemed to show, however, that the mode of operation of such detectors differed considerably from that of the more ordinary crystal detectors, the type of curves obtained more resembling those of the electrolytic and other detectors in which very little agreement could be traced between the sensitiveness and differential curves. The response of the detector under oscillations seemed in this case to resemble that of a filings coherer, again suggesting something in the nature of a "trigger" action. In reply to Mr. Duddell and Prof. Howe steps were taken in the tests to ascertain to what extent the characteristic curves could be repeated, and it was found that with the "good contact" detectors, or those operating with moderately firm contact between the crystals, *e.g.*, the "Perikon," almost exact repetition of the curves could be obtained on different occasions, and that although changing the crystals or points of contact altered the scale of the curves, yet in general the main features were present. With the more "imperfect," or "loose-contact," detectors, however, the repetitions were

not nearly so good. The curve shown by Mr. Owen was of interest, but really expressed the response of a detector to signals of various strengths, and did not give the sensitiveness as defined in the paper. In reply to Mr. Rayner, the resistance of the detectors at their points of maximum sensitiveness varied from a few hundred to about 10,000 ohms or more, depending on the crystals used.

Mr. W. DUDELL, F.R.S., exhibited a Water Model of the Musical Electric Arc.

In the model the arc is represented by a mushroom valve. The pressure of the valve on its seat is so arranged that the pressure tending to re-seat the valve diminishes very rapidly as the valve lifts. Water is admitted beneath the valve, flows through the valve into the vessel which contains it, and overflows. In order to indicate the difference of pressure on the two sides of the valve which represents the arc a glass pressure column is introduced into the pipe leading to the valve and quite close to it. As the water overflows freely from the tank in which the valve is immersed, the pressure on this side of the valve may be taken as our zero of reference, and consequently the height of the water column in the pressure tube above or below the level of the overflow gives the pressure underneath the valve.

If water be admitted below the valve the pressure in the pressure tube rise to a high value; finally the valve lifts, i.e., the arc is struck, but the pressure still remains high. If, however, the flow of water is increased, the valve will open considerably and the pressure below it will decrease. If nicely adjusted this effect can be made to take place over a considerable range.

If instead of connecting a pressure tube of small bore indicating the pressure on the underneath side of the valve a large diameter tube be introduced so that the water column in it has a periodic time of its own and is able to oscillate similarly to the condenser circuit shunting the arc, oscillations will be set up in this column, and if the periodic time of the liquid in this column be altered, the period of the oscillations will be altered; this can easily be done by connecting air vessels of different capacity to the open end of the tube, so altering the controlling force acting on the water, in other words altering the capacity of the circuit shunting the arc.

With this water model a great many of the properties of arcs both intermittent and oscillating can easily be shown. The one point of difficulty in constructing the model is to obtain a force acting on the valve which decreases rapidly when the valve lifts and which occasions no friction. So far the only successful method which the author has tried is to hang from the underneath side of the valve a piece of soft iron which nearly touches the pole of a small electromagnet. This gives a force which without any friction rapidly decreases as the valve lifts and works very well.

Mr. C. R. DARLING, A.R.C.S., exhibited some "Further Experiments with Liquid Drops and Globules."

The experiments included a demonstration of the structure of a liquid jet by means of orthotoluidine (density slightly greater than x at room temperature) issuing from an orifice under water; the formation of spheres of water enclosed in a skin of aniline and of spheres of dimethyl-aniline encased in a skin of water; the expansion of a globule of liquid floating on water when a drop of another liquid is allowed to fall on it, and the combination of globules of certain liquids when floating on water. This was well marked in the case of a globule of dimethyl-aniline and a number of smaller globules of orthotoluidine.

A paper entitled "*A Note on Aberration in a Dispersive Medium, and Airy's Experiment*," by Mr. JAMES WALKER, was taken as read.

The view recently adopted by Lord Rayleigh that in the case of aberration we are concerned with the group-velocity instead of with the wave velocity, makes it necessary to consider the experiment of Airy, in which he measured the angle of aberration with a telescope filled with water.

A modification of Lord Rayleigh's explanation of this

experiment leads to the result that the angle of aberration thus determined corresponds to an angle $\mu - v/U$ measured in air. The same result is obtained from an analytical investigation, and a numerical calculation shows that the increase in the angle is about 1 per cent—an amount that is probably too small to be detected.

NOTICES OF BOOKS.

Outlines of Theoretical Chemistry. By FREDERICK H. GETMAN, Ph.D. (Johns Hopkins). New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1913.

THE possession of a working knowledge of elementary physics and chemistry has been presupposed in the students who use this book, although an introductory chapter gives a review of the main principles with which they should be familiar. The theory of electrons is discussed very clearly in an early chapter, which appears in some ways rather out of place, although the reading of it could be postponed until after the chapters on the gas laws, liquids, solids, solutions, &c. Radio-activity is not included, the author believing that the condensed account, which would be all that limitations of space would allow, would not be of sufficient value to justify its insertion. The book is evidently the work of an experienced teacher, and is well written. An error in the diagram illustrating the migration of the ions, which will make the text very difficult to follow by an uninitiated student, will require correction in a second edition.

Quantitative Analysis by Electrolysis. By ALEXANDER CLASSEN, with the Co-operation of H. CLOEREN. Translated from the Fifth German Edition by WILLIAM T. HALL. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1913.

THE fifth German Edition of this work has undergone such extensive alteration that for the new English edition practically a fresh translation had to be made. Many advances have been made in quantitative electrolytic work, both in theory and practice, and the author has recently worked out the details of many new rapid methods, which are duly noted in the text. The equipment of the author's laboratory at Aachen is fully described, and directions are given for the estimation and separation of all the more important elements. Some clumsy expressions mar the style of the text; for example, "acts somewhat differently than," "behave similar to." "The current must be kept at 0.35 volts" is evidently a slip.

Second Report to His Majesty's Secretary of State for the Home Department on the Draft Regulations Proposed to be made for the Manufacture of Patent Fuel (Briquettes) with the Addition of Pitch. By ALFRED HERBERT LUSH. London: Darling and Son, Ltd.

THIS second report on the regulations suggested for adoption in the manufacture of patent fuels (briquettes) with the addition of pitch gives a summary of the former report and an account of the resumption of the enquiry. The action of employers made in response to the circular of November, 1911, is dealt with, and the measures adopted to remedy some defects and to safeguard the health of the employees in some minor respects are described. No definite evidence as to the results of these measures can be adduced. The work of Dr. Ross on the "Origin of Cancer" is described in outline in the report, and the question of the elimination of the injurious constituent in pitch is discussed in some detail. Since the Commissioner recognises that the objects of the issue of the Draft Regulations might be effected more satisfactorily by removing the auxetics and kinetics in pitch than by enforcing the regulations, he finally recommends that they be withdrawn.

Die Atome. ("The Atom"). By JEAN PERRIN. Authorised German Translation by Dr. A. LOTTERMOSER. Dresden and Leipzig: Theodor Steinkopff. 1914. (Mk. 5).

THIS book should be carefully read by all who are interested in modern developments of theories of the constitution of matter and of the nature of the atom. Prof. Perrin's pioneer work in the proof of the actual existence of the molecules is already known to readers of the CHEMICAL NEWS, who will be interested to study in the book further details and the historical development of the problem. The author's aim is broadly "to explain the complicated visible by the simple invisible," and in particular to establish within narrow limits the actual value of Avogadro's constant N , the number of molecules in the grm.-molecule. After a description of the experimental details and an account of the theories underlying the many different methods of arriving at this result, the actual values obtained are tabulated. They show a very remarkable agreement, and the unbiased reader will find himself bound, whatever prejudices he may have started with, to agree with the author that—"The atomic theory has triumphed, but the atom is no longer to be regarded as an eternal indivisible entity, but as a limitless universe of new worlds, the investigation of which will bring many striking and unforeseen results to light."

Der Heutige Stand der Synthese der Pflanzenalkaloiden. ("The Present Position of the Synthesis of the Plant Alkaloids"). By Dr. HUGO BAUER. Braunschweig: Friedrich Vieweg und Sohn. 1913. (Mk. 4.50).

IN the synthesis of the plant alkaloids problems of very great difficulty have to be solved, and methods hitherto unknown in organic chemistry have had to be worked out for the purpose. This book, which is the fifty-first volume of the "Wissenschaft" series, gives a clear summary of the results which have so far been obtained. The properties and reactions of the alkaloids as a class are first described, and then the methods adopted for the synthesis of individual members of the various groups are given in full. The text is always clear and concise, and workers in this region will find the book a very useful work of reference.

Handbuch der Arbeitsmethoden in der Anorganischen Chemie. ("Handbook of Practical Methods in Inorganic Chemistry"). Vol. III. Part I. Edited by Dr. ARTHUR STÄHLER. Leipzig: Veit and Co. 1913.

THIS volume describes methods of taking physico-chemical measurements, such as the determination of vapour densities, critical constants, specific heats, &c., and includes a lengthy article on metallography. The theory of the methods described is given, as well as full practical details, and no other book rivals it as far as comprehensiveness is concerned. It contains nearly 700 pages and over 350 illustrations, and every large laboratory should possess a copy for reference.

Nouvelles Orientations Scientifiques. ("New Scientific Orientations"). By FERNANDO ALSINA. Translated from the Catalan by J. PIN Y. SOLER. Paris: Garnier Frères.

ALTHOUGH the author of this book writes temperately and with restraint he makes rather heavy demands upon his reader's faith in his experiments and his deductions from them, when he claims that he has proved that the conceptions of the forces of affinity, cohesion, attraction, polarity, &c., are entirely false. He states that all the phenomena in which such forces are supposed to come into play can be explained by supposing that they are due to the intimate relation between the movements of the ponderable particles of matter and the movements of the ether. The author was encouraged to undertake his researches by Tyndall, and he appears to have given much time and thought to the experimental work which he describes shortly in this book.

Guide pour les Manipulations de Chimie Biologique. ("Guide to Experimental Work in Biological Chemistry"). By GABRIEL BERTRAND and PIERRE THOMAS. Second Edition. Paris: H. Dunod and E. Pinat. 1913.

THIS book contains the details of a large number of practical exercises dealing with the composition of living organisms, diastases, and ferments. Volumetry, microscopic work, and the use of the polarimeter and spectroscope are described, and full directions are given for many qualitative and quantitative experiments with which the student of biological chemistry should be familiar. In the second edition the chapters which have been most largely modified or augmented are those on the acids, alkaloids, proteins, and diastases, and in addition some experiments on the synthetic phenomena brought about by the living organism have been inserted.

Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie. ("New Conceptions in the Realm of Inorganic Chemistry"). By Prof. Dr. A. WERNER. Third Edition. Braunschweig: Frederick Vieweg und Sohn. 1913. (11 Mk.).

A CONSIDERABLE amount of new material has been added to the third edition of this book, which gives a unique survey of the chief theories of inorganic chemistry. The most important additions have been made in the special part which deals with the constitution of inorganic compounds, and which has been very much enlarged by descriptions of recent experimental work. The theories of valency put forward by the author and other workers are lucidly discussed, and the very great advances which have been made during the last five years in our knowledge of the chemistry of complex substances are admirably reviewed.

The Purification of Public Water Supplies. By GEORGE A. JOHNSON. Washington: Government Printing Office. 1913.

THIS bulletin has been written in order to provide officials and citizens with a simple and straightforward statement of the principles and practices governing the purification of waters used for domestic purposes. American methods are principally discussed, but those who are interested in water purification in this country will be able to acquire a good deal of information from the pamphlet. A short historical account of water purification is included, and the method of sterilisation by means of sodium hypochlorite which has been developed in recent years is also discussed. The problems of municipal water softening are shortly treated, and details of the methods of filtration employed in many towns are given.

CORRESPONDENCE.

INSTITUTE OF CHEMISTRY CONFERENCE.

To the Editor of the Chemical News.

SIR,—The letter by Mr. Wilberforce Green in your issue of January 30 comes very near to the most immediately important point for most practising chemists. Professional unity is in any case essential, but we must realise from the outset that the main condition of work of most chemists—namely, whole-time employment by industrial concerns or public departments—are fundamentally different from those of the members of the already recognised professions, such as medicine and law. Just as medical men are already realising, through the British Medical Association, that changing conditions of medical work need altered methods of organisation and professional activity, so chemists must realise now that their special conditions of work involve, if chemists are to take their deserved position in the community, an organisation whose aim and methods shall be specially adapted to those conditions, and not slavishly copied from other professions.

The need of the chemist, the metallurgist, and the physicist is for an Association which aims clearly at the organisation of *all* scientific technologists for the purpose of controlling the conditions of work, the pay, and the methods of entry into the profession, and I am glad to see that Mr. Green, as Secretary of the Association of Chemical Technologists, recognises the need for including "all those who are actively and personally engaged in applied chemistry." Unless chemists determine to work together for this end they will fail both to develop that professional status to which the national importance of their work entitles them, and to obtain such remuneration as will enable them adequately to support that status.—I am, &c.,

RICHARD MATHER.

6, John Street, Adelphi, W.C.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clvii., No. 24, December 15, 1913.

This number contains no chemical matter.

No. 25, December 22, 1913.

Absorption of Ultra-violet Rays by Alkaloids of Morphine Group and by Phenanthrene.—M. Gompel and Victor Henri.—The absorption curve of phenanthrene can be decomposed into three regions, the first of which ($\lambda=3800-3050$) shows five absorption bands, the second two, and the third one very strong band at $\lambda=2503$. The absorption curves of morphine and codeine are almost identical, but that of codeine is rather higher than that of morphine. The curve of apomorphine is very much like the phenanthrene curve, and is very different from the morphine curve. The strong phenanthrene band is missing in apomorphine, and hence it is probably due to the double bond between the 9 and 10 carbons, which double bond is saturated in apomorphine.

Catalytic Etherification in the Wet Way.—F. Bodroux.—The power of yielding ether salts in favourable conditions, in presence of an acid catalyst and water, is peculiar to certain monobasic acids of simple function and to primary saturated alcohols of the aliphatic series. The author thinks that most probably an addition product of

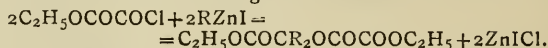
formula $\text{R}-\begin{array}{c} \text{OH} \\ \diagup \\ \text{C}-\text{OH} \\ \diagdown \\ \text{X} \end{array}$ is formed as an intermediate product, XH being any mineral acid.

Supposed Separation of Radium D from Lead by Grignard's Reaction.—Charles Staehling.—Hofmann and Wölfl have stated that they have effected the separation of radium D from lead in active lead by means of Grignard's reaction. Tetraphenyl lead can be prepared by allowing phenyl magnesium bromide to react with lead chloride, and when active lead was used Hofmann and Wölfl thought they had shown that the radium D did not enter the organic compound, but it was concentrated in the lead: $2\text{PbCl}_2 + 4\text{C}_6\text{H}_5\text{MgBr} = (\text{C}_6\text{H}_5)_4\text{Pb} + \text{Pb} + 4\text{MgClBr}$. The author has repeated the experiments but cannot confirm these results, and can find no indication of a separation of the radium D from the lead.

Vacuum Tar.—Amé Pictet and Maurice Bouvier.—By treatment with sodium the authors have proved that vacuum tar contains alcohols, probably of the hydroaromatic series. By fractionation and removal of these alcohols by means of sodium they have obtained different fractions, two of which they have investigated. One consists of a hydrocarbon of formula $\text{C}_{10}\text{H}_{20}$, which appears to be the exahydride of durene (1.2.4.5-tetramethylcyclohexane),

while the other, of formula $\text{C}_{11}\text{H}_{22}$, has not yet been definitely identified, but may probably be the hexahydride of pentamethyl benzene.

Syntheses by Means of Organometallic Derivatives of Zinc. Preparation of α -Ketonic Acids.—E. E. Blaise.—It might be supposed that the α -ketonic ethers could be prepared by the action of the chloride of ethoxalyl on the mixed organometallic derivatives of zinc, but as a matter of fact the following reaction occurs:—



The indirect method of preparing the α -ketonic ethers which the author has previously described, and in which the cycloacetals are formed as intermediate products, gives good results. Thus oxyisobutyric acid is treated with ethoxalyl chloride and the raw product is heated with thionyl chloride. The condensation of the acid chloride thus obtained with a mixed organometallic derivative of zinc gives the mixed cycloacetal of the α -ketonic acid. The alcoholysis of the cycloacetal gives a mixture of oxyisobutyric ether and α -ketonic ether, which can easily be separated by fractionation.

Synthesis of Benzyl Chloride and its Homologues.—Marcel Sommelet.—When the chlorinated ether oxides $\text{ClCH}_2\text{OCH}_3$, $\text{ClCH}_2\text{OC}_2\text{H}_5$, $\text{ClCH}_2\text{OC}_3\text{H}_7$ react with benzene in presence of aluminium chloride below 0° , hydrochloric acid is evolved and the ether oxide of a benzyl alcohol is formed: $\text{RH} + \text{ClCH}_2\text{OR}' = \text{RCH}_2\text{OR}' + \text{HCl}$. At the same time some benzyl chloride is formed by the reaction $\text{C}_6\text{H}_6 + \text{C}_3\text{H}_7\text{OCH}_2\text{Cl} = \text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{C}_3\text{H}_7\text{OH}$. It is necessary to dilute with carbon disulphide. With toluene SnCl_4 has to be used instead of aluminium chloride. The reaction is applicable to many benzene hydrocarbons. Toluene gives rise to the chloride of paratoluyll, and generally speaking the substitution takes place every time it is possible in the para position with reference to a side chain.

MEETINGS FOR THE WEEK.

MONDAY, 16th.—Royal Society of Arts, 8. (Cantor Lecture). "Artistic Lithography," by Joseph Pennell.

TUESDAY, 17th.—Royal Institution, 3. "Animals and Plants under Domestication," by Prof. W. Bateson, F.R.S., &c.

WEDNESDAY, 18th.—Royal Society of Arts, 8. "Preservation of Wood," by John Slater, F.R.I.B.A.

— Biochemical Society, 5.30. (In the Chemical Dept., Guy's Hospital Medical School).

THURSDAY, 19th.—Royal Institution, 3. "Hamlet in Legend and Drama," by Prof. I. Gollancz, Litt.D.

— Royal Society. "Brain of Primitive Man, with special reference to the Cranial Cast and Skull of Eoanthropus (the Pittdown Man)," by G. Elliot Smith. "Oxidases," by A. J. Ewart. "A New Malaria Parasite of Man," by J. W. W. Stephens. "Investigations dealing with the Phenomena of 'Clot' Formations—Part II., The Formation of a Gel from Cholate Solutions having many Properties analogous to those of Cell Membranes," by S. B. Schryver. "Influence of the Position of the Cut upon Regeneration in *Gunda ulvae*," by D. Jordan Lloyd.

— Chemical, 8.30. "Condensations of Cyanohydrins—Part II., The Condensation of Chloralcyanohydrin with Chloral Hydrate and with Bromal Hydrate," by H. L. Crowther, H. McCombie, and T. H. Reade. "The System Ether—Water—Potassium Iodide—Mercuric Iodide: Part II., Saturated Solutions in the Four-component System," by A. C. Dunningham. "Connection between the Dielectric Constant and the Solvent Power of a Liquid," by W. E. S. Turner and C. C. Bissett. "Viscosities of some Binary Liquid Mixtures containing Formamide," by E. W. Merry and W. E. S. Turner.

FRIDAY, 20th.—Royal Institution, 9. "Busts and Portraits of Shakespeare and of Burns—an Anthropological Study," by Prof. A. Keith, F.R.S., &c.

— Physical, 8. "Moving Coil Ballistic Galvanometer," by R. L. Jones. "Vibration Galvanometers of Low Effective Resistance," by A. Campbell. "Vacuum-tight Lead-seals for Sealing-in-wires in Vitreous Silica and other Glasses," by H. J. S. Sand.

SATURDAY, 21st.—Royal Institution, 3. "The Electric Emissivity of Matter," by J. A. Harker, F.R.S., &c.

THE CHEMICAL NEWS.

VOL. CIX., No. 2830.

THE PLACE OF MERCURY IN THE PERIODIC SYSTEM.

By PRAFULLA CHANDRA RAY.

MERCURY is assigned a place in the periodic system in Group II., and regarded as a member of the magnesium-zinc family of elements. Mercuric compounds, no doubt, bear some analogy to those of magnesium, zinc, and cadmium, though by no means is it so very close. Mercury, for instance, is far less electro-positive than cadmium or zinc. Magnesium and zinc chlorides undergo hydrolysis in aqueous solution, and when evaporated to dryness give rise to basic salts with evolution of hydrochloric acid. The halides of cadmium, however, resemble the corresponding compounds of mercury as far as the non-dissociation of their aqueous solutions is concerned; moreover, cadmium, like mercury, seems to yield a lower oxide and a chloride. (Cadmous chloride and oxide have evidently been obtained in an impure condition; *vide* Morse and Jones, *Am. Chem. Journ.*, 1890, xii., 488; *cf.* Canzoneri, *Gazzetta*, 1897, [2], xxvii., 486). A zincose-zincic chloride has also recently been prepared in my laboratory by Datta and Sen (*Journ. Am. Chem. Soc.*, June, 1913, xxxv.).

As might be expected from its feeble ionisation, cadmium chloride shows many properties in common with mercuric chloride, notably its capacity to combine with ammonia and the amines, including pyridine and piperidine (Veret, *Comptes Rendus*, 1892, cxv., 464; *cf.* also Ray and Dhar, "Chlorides of the Mercurialkyl Ammonia Series, &c.," *Journ. Chem. Soc.*, 1913, ciii., 3).

While the relationship of the compounds of diad mercury with those of the zinc-cadmium family is by no means very marked, mercurous compounds, on the other hand, bear the closest analogy to those of silver. As far as the halides are concerned this similarity has been noticed for a long time past. The most noticeable feature in this respect is that afforded by mercurous nitrite, both in its properties and in its mode of formation. As long ago as 1874, Russell noticed that when silver dissolves in nitric acid silver nitrite is formed in quantity, partly in solution in the silver nitrate liquor, partly as crystals (*Journ. Chem. Soc.*, [2], xii., 3). The stability of silver nitrite in presence of strong nitric acid is noteworthy, as ordinary nitrites are decomposed even by the weakest acids. Mercurous nitrite also is produced under similar conditions; indeed, the initial product of the action of dilute nitric acid upon mercury in the cold is the nitrite and not nitrate (Ray, *Zeit. Anorg. Chem.*, 1896, Bd. xii., 365; *Journ. Chem. Soc.*, 1897, 337), and the former is quite stable in presence of a concentrated solution of mercurous nitrite and nitric acid (*cf.* Ray, "Theory of Production of Mercurous Nitrite, &c.," *Journ. Chem. Soc.*, 1905, lxxvii., 171).

Both in its chemical and physical properties, again, mercurous nitrite has been found to be the analogue of silver nitrite. So far it has been known to be the only other metallic nitrite which, with ethyl and other alkyl iodides, yields nitro-bodies of the fatty series (Ray, *Ann.*, cccxvii., 253; *Proc. Chem. Soc.*, 1899, p. 239); in fact, it can be used as an efficient substitute for silver nitrite.

The colour of compounds is often found to be a periodic function of the atomic weights of the component elements (Bayley, *Phil. Mag.*, 1882, xiii., 34). Thus silver chloride is white, while the bromide has a faint yellow tint, and the iodide is distinctly yellow. The corresponding halides of mercury also show the same relative intensity in a more pronounced manner. For example, mercurous chloride is white, the bromide yellow (mercurous bromide is often

described as white, *cf.*, Strohmman, *Ber.*, 1880, xx., 2818, but its yellow colour under modified conditions has been noticed; *e.g.*, the crystalline needles are "jaunes à chaud blanchâtres à froid," Moissan, *Chim. Miner.*, T. v., 256), and the iodide intensely yellow (Ray, *Journ. Chem. Soc.*, 1897, p. 350). Silver nitrite has a pale yellow tint, but mercurous nitrite has a deep bright yellow colour. Silver and mercurous hyponitrites also show a similar gradation in the depth of colour.

In assigning the proper place to an element in the periodic system isomorphism is often an important help and guide. According to Groth the univalent metals, copper, silver, and gold, in the form of the crystallised elements, constitute an undoubtedly isomorphous group, and the first two replace each other isomorphously in a number of native silver compounds, as also in the complicated salts; the triple thiocyanates, $\text{Cs}_3\text{SrCu}_2(\text{SCN})_7$ and $\text{Cs}_3\text{SrAg}_2(\text{SCN})_7$, and the compounds—

NH_4Cl , $\text{CuCl}_4(\text{NH}_4)_2\text{S}_2\text{O}_3$ and NH_4Cl , $\text{AgCl}_4(\text{NH}_4)_2\text{S}_2\text{O}_3$ ("Chemical Crystallography," trans. by Marshall, p. 73). As far as one can make out, no compound of monad gold has as yet been described in which it isomorphously replaces silver or monad copper. From the close similarity of the compounds of silver to those of monad mercury as shown above, it might have been reasonably expected that they should vicariously replace each other in some cases. This expectation has also been realised. In the complex silver-mercurousmercuric oxynitrates, silver isomorphously replaces univalent mercury (Ray, *Journ. Chem. Soc.*, 1907, xci., 2033).

It will thus be noticed that while the relationship of gold with silver and mercury is at best very remote, that of monad mercury with silver is all along very close and marked. It would appear to be more rational to place monad mercury at the bottom of Group I. in the periodic system and relegate gold to its more congenial place in Group VIII. immediately after platinum. Univalent mercury should be regarded as quite a distinct metal from bivalent mercury; the former is related by ties of closest affinity to silver, while the latter can, at best, claim weak kinship with members of the second group, namely, zinc and magnesium. (It is, of course, not suggested that diad mercury should altogether be removed from its place in Group II.). In this duality of functions mercury is comparable to thallium, which, with variation in valency, affords also a remarkable instance of variation in chemical properties.

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NITROGEN AND CHLORINE IN RAIN AND SNOW.

By G. H. WIESNER.

SHUTT determined the nitrogen in the rain and snow that fell near Ottawa, Canada, during a portion of the year 1906—07. It occurred to us it might be worth while to examine the precipitations at Mount Vernon, Iowa. It is a village of 1700 inhabitants, without manufacturing industries, rather sparsely populated, so that the atmosphere is reasonably free from contamination.

The rain and snow were collected in two porcelain lined pans, each 20 inches in diameter, in an open space near the centre of the village. We tested altogether 31 samples, 22 of rain and 9 of snow.

The snowfall during this period amounted to 24 inches (two precipitations were snow and sleet), which is equivalent to 2 inches of rain. The rain during the period was 14 and eight-tenths inches, making a total of 16 and eight-tenths inches, which is above the normal precipitation for this section.

TABLE I.

Date.	Precipitation in inches.		Parts per million.				
	Snow.	Rain.	Nitrogen in nitrite.	Nitrogen in nitrate.	Chlorine.	Free ammonia.	Albuminoid ammonia.
Feb. 22	Sleet and snow	0.25	0.0035	0.15	4.8	6.00	7.00
25	3.0	—	0.002	0.13	3.2	1.28	1.92
Mar. 4	0.5	—	0.0035	0.35	4.8	7.0	8.0
5	1.0	—	0.003	0.36	7.2	5.0	5.5
7	4.0	—	0.0025	0.13	4.4	3.4	3.75
12	—	0.25	0.004	0.6	8.0	10.0	14.0
13	—	0.5	0.002	0.15	2.8	3.75	1.0
13	—	0.1	0.002	0.14	4.8	0.4	0.56
14	3.0	—	0.0015	0.11	5.2	1.0	1.0
20—21 ..	5.0	—	0.001	0.09	4.0	5.0	6.0
23	—	1.0	0.002	0.27	5.2	0.48	0.76
April 2	—	0.4	0.0015	0.24	6.0	0.68	1.12
4	1.25	—	0.002	0.25	2.0	0.96	0.96
7	Snow and rain	0.5	No trace	0.15	4.8	0.52	0.44
8	—	0.8	"	0.1	4.8	0.4	0.4
9	—	1.0	"	0.06	3.6	0.224	0.44
10	—	0.05	Not tested	0.15	4.0	0.36	0.2
May 3—4 ..	—	0.75	0.004	0.45	4.8	0.32	0.32
4—5	—	1.25	0.002	0.1	4.8	0.15	0.32
5	—	1.0	No trace	0.09	4.8	0.112	0.36
8—9	—	0.5	0.001	0.11	4.4	0.04	0.8
13	—	0.5	0.002	0.1	4.0	0.48	1.8
14	—	1.0	0.001	0.08	4.0	0.36	0.32
15	—	1.0	No trace	0.05	4.8	0.32	0.2
17	—	0.1	Not tested	0.07	4.0	1.0	0.36
19—20 ..	—	0.5	0.004	0.11	5.2	0.36	0.34
20	—	0.5	0.002	0.09	4.4	0.2	0.36
20—21 ..	—	0.5	0.0015	0.06	4.8	0.136	0.112
24	—	0.1	Not tested	0.1	Not tested	0.24	0.16
25—26 ..	—	2.0	0.001	0.08	4.8	0.112	0.36
June 5	—	0.75	0.001	0.2	4.0	0.36	0.75

TABLE II.

Date.	Precipitation in inches.		Pounds of nitrogen per acre.				
	Snow.	Rain.	Nitrogen in nitrite.	Nitrogen in nitrate.	Nitrogen in free ammonia.	Nitrogen in albuminoid ammonia.	Total.
Feb. 22	Snow and sleet	0.25	0.00019	0.0085	0.2802	0.32690	0.61579
25	3.0	—	0.00011	0.00687	0.05979	0.08668	0.15655
Mar. 4	0.5	—	0.00044	0.00330	0.00544	0.06622	0.07540
5	1.0	—	0.00005	0.00676	0.07785	0.08563	0.17029
7	4.0	—	0.00018	0.00983	0.21179	0.23356	0.44536
12	—	0.25	0.00022	0.03378	0.46712	0.69397	1.15509
13	—	0.5	0.00022	0.01701	0.35034	0.09342	0.46099
14	3.0	—	0.00008	0.00623	0.04671	0.04671	0.09973
20—21 ..	5.0	—	0.00009	0.00850	0.38945	0.46710	0.86504
23	—	1.0	0.00045	0.06126	0.08968	0.14574	0.29713
April 2	—	0.4	0.00013	0.02178	0.05082	0.08370	0.15643
4	1.25	—	0.00004	0.00567	0.01793	0.01793	0.04157
7	Snow and rain	0.5	No trace	0.01701	0.04735	0.02055	0.08492
8	—	0.75	"	0.01715	0.05979	0.05979	0.13673
9	—	1.0	"	0.01361	0.04185	0.08221	0.13767
10	—	0.05	Not tested	0.00170	0.00306	0.00186	0.00662
May 3—4 ..	—	0.75	0.00068	0.07582	0.04484	0.04484	0.16618
4—5	—	1.25	0.00056	0.02535	0.03440	0.07474	0.13506
5	—	1.0	No trace	0.02041	0.02097	0.06726	0.10864
8—9	—	0.5	0.00011	0.01257	0.00373	0.07474	0.09115
13	—	0.5	0.00022	0.01134	0.04484	0.16816	0.22456
14	—	1.0	0.00022	0.01815	0.07726	0.05979	0.15542
15	—	1.0	No trace	0.01134	0.05979	0.03737	0.10850
17	—	0.1	Not tested	0.00588	0.01868	0.00772	0.03228
19—20 ..	—	0.5	0.00045	0.01257	0.03863	0.03176	0.08341
20	—	0.5	0.00022	0.01020	0.01868	0.02863	0.05773
20—21 ..	—	0.5	0.00017	0.00680	0.01269	0.01046	0.02912
24	—	0.1	Not tested	0.00226	0.00448	0.00298	0.00972
25—26 ..	—	2.0	0.00045	0.03630	0.04385	0.15453	0.19752
June 5	—	0.75	0.00017	0.03403	0.05794	0.10510	0.18724
			0.00549	0.52412	2.70291	3.35291	6.58543

The samples were collected from February 22 to June 5, 1912. The winter months were dry up to the time the investigation was begun.

The snow of March 4 was taken from drifts on the hard crusts of the previous fall, and was not very clean. This may account for the large amount of both free and albuminoid ammonia.

The rain of March 12 was accompanied by the first thunderstorm, and the nitrogen nitrate was 0.6 part per million, the free ammonia 10 parts, and the albuminoid ammonia 14 parts. These were the highest results obtained from any sample. After this the rains were frequent until April 10. Then there was a dry period of nearly a month, and the rain of May 3 had 0.45 part of nitrogen nitrate per million. Beginning May it rained three days, and the samples were tested in three portions. The third portion had only 0.09 part of nitrogen nitrate per million, and no trace of nitrite. In general, the various substances in solution depend on the time between precipitations. The chlorine remained the same in the three precipitations, 4.8 parts per million.

In determining the nitrogen in ammonia it was computed that 1 inch of rainfall per acre weighs 226,875 pounds. Then, if the precipitation contained 0.04 part of ammonia per million, the weight expressed as millionths was multiplied by 0.04 and the product by 14/17, which gives the nitrogen in pounds per acre.

The average of the free ammonia in snow was 3.35 parts per million and in the rain 0.931 part per million.

The albuminoid ammonia in snow was 3.84 parts per million and in rain 1.13 parts per million.

The nitrogen nitrite in snow was 0.0021 part per million and in rain 0.0018 part.

In snow the average for the nitrates was 0.19 part per million and in rain 0.15 part.

The average of the chlorine in snow was 4.7 parts per million and 4.8 parts per million. The source of this is doubtless the sodium chloride from the Atlantic Ocean. As the spray is washed upon the shore it is caught by the wind and borne across the continent. Mount Vernon is about 1200 miles distant from the Atlantic Ocean.

Table I. shows the parts per million of the several constituents, and Table II. the number of pounds per acre. The total number of pounds of nitrogen per acre during the period covered by the investigations was 6.26887.

We desire to express our thanks to Dr. N. Knight for the aid he rendered in this work.

Cornell College, November 22, 1913.

THE MECHANISM OF ANODIC REACTIONS AND THE BEHAVIOUR OF IRON AND NICKEL ANODES.*

By E. P. SCHOCH,
Professor of Chemistry in the University of Texas.

(Concluded from p. 76).

In the absence of any "oxide skeleton" the layer of oxygen, on thickening, would soon allow bubbles of gas to escape—as is probably the case with platinum, iridium, &c., in which the oxide formed is within the body of the metal. But when a non conducting oxide skeleton is formed the layer of gas may accumulate to a relatively great thickness as the oxide skeleton grows, and this may prevent more or less completely the passage of any ions to the electrode. (However, such a film will still allow free electrons to pass from the electrode to the solution, which gives the pole the property of an electric valve). Finally, if the oxide is oxidisable to a conducting

(per-)oxide, then a suitable concentration of oxygen produced by its discharge under a sufficiently great potential will produce this peroxide, and oxygen gas will then be evolved from the new surface of the peroxide. The actual existence of this latter state of affairs has been beautifully demonstrated by E. Mueller (*Zeit. Elektrochem.*, xiii., 133), who showed that a copper anode in sodium hydroxide solution forms hydrated cuprous oxide as long as the current density is small enough; but with a larger current density the anodic potential becomes more noble, copper peroxide is visibly formed on the anode, and then oxygen is evolved from the surface of the latter. It appears that the "oxygen producing" discharge of ions on peroxide anodes is a rapid reaction, because no great hindrance is observed even with great current densities.

This beautiful demonstration by E. Mueller of the relations between active and passive copper indicates that the phenomena which characterise the attainment of passivity by some metals in certain electrolytes appears to be nothing but the regular behaviour of anodes under the existing conditions. The writer's study of the behaviour of iron and nickel anodes in various electrolytes has led him to the same conclusion with reference to the passivity of these metals. These facts will now be reviewed in the light of the general theory of anode actions outlined above.

Iron or nickel placed in solutions of their (neutral) salts will assume a definite "equilibrium" potential (*Zeit. Physik. Chem.*, lviii., 301; *Am. Chem. Journ.*, xli., 208).

When such electrodes are used as cathodes during electrolysis alloys of iron or nickel with hydrogen are obtained which exhibit higher (more zincic!) potentials than the equilibrium potentials of the metals.

When such electrodes are used as anodes during electrolysis, with current densities below a certain approximate limit, then only dissolution of the metal will occur, and with any one particular current density the anodic polarisation (or potential drop below the equilibrium potential) will be the same whether the particular current density is approached through a series of increasing or decreasing current densities (in the latter case even the largest current densities in the series must not have exceeded the "limit" mentioned above). In other words, current densities within this limit do not leave a "permanent" effect upon the surface of the electrode. With an electrolyte containing any one particular anion the approximate limit of these current densities which do not leave a permanent effect upon the anode is extended to greater current densities by (a) raising the temperature, (b) an increase in the concentration of the hydrogen ions or a decrease of the hydroxyl ion, (c) by stirring or replenishing the electrolyte on the surface of the anode. Hence the writer's experiments were made at different temperatures—most of them at 25° C., and a few at 98° C.; the concentration of the hydrogen ion was definitely known and varied from one-tenth normal acid to one-tenth normal alkali; and in all experiments the electrolyte was stirred vigorously and uniformly, and in the experiments with iron fresh electrolyte was also passed constantly through the anode chamber in order to avoid the complicating oxidation of the ferrous salt formed (*Journ. Phys. Chem.*, xiv., 739; *Am. Chem. Journ.*, xli., 235).

The particular electrolytes employed were (a) neutral solutions of ferrous or nickel sulphate and chloride, solutions of potassium sulphate, nitrate, perchlorate, chlorate, bromate, iodate, chromate, hydroxide, and sodium acetate; (b) acidified and alkaline solutions of the sulphates, nitrates, and acetates; and (c) mixtures of sulphate with chromate and sulphate with fluoride. Arranged in increasing order of their limits of the current densities with which the surfaces of iron or nickel anodes are not "permanently" affected, the anions present the following list:—

- (a) Hydroxides, iodates, bromates, chlorates, chromates, with all of which only exceedingly small current

* A Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, November 12, 1913.

densities do not affect the surface of the anode permanently.

- (b) Nitrates.
- (c) Perchlorates.
- (d) Acetates.
- (e) Sulphates.
- (f) Halides—with the latter large current densities do not affect the surface.

With current densities beyond such limits, the action of the current produces a *permanent* effect—that is, the effect remains for a finite period of time after the current has ceased to flow, and with the same current density an iron or a nickel pole may show widely different potentials depending on its "previous history" in an uncontrollable manner. In general, it may be said that the potential of the electrode will become lower (more noble!) with the length of time that such current densities beyond the above limit continue to flow, and the potential drop will be more rapid with greater current densities than with lesser. In many cases the potential will drop almost suddenly down to the potential with which oxygen is evolved. When the surface of an electrode has been affected by electrolysis with a current density beyond the "limit" above, then an exceedingly small current density will suffice to keep its potential steady—that is, will suffice to maintain the electrode surface in the state in which it is. But when the current ceases to pass, the iron or nickel electrode immediately begins to lose its permanent effect in *all electrolytes*, and it is only a question of time until the surface is again in its original state.

These are the general facts in the behaviour of iron or nickel anodes in various electrolytes. They are readily explained by the general theory of anode action, as follows:—

With current densities below the limit mentioned, the ions are discharged upon the electrodes, where they react with velocities depending on the specific relation between each anion and each metal. When the surface of the anode is covered with discharged anions which are still in the progress of reaction, access of other anions to the surface is impeded, and the production of oxygen ions near the electrode will begin. The discharge of the latter upon the metal surface produces the permanent effect; and anything that will delay or hinder the formation of these oxygen ions will widen the limit of the current densities which do not affect the surface. An increase of temperature, as usual, will increase the velocity of reaction between the anions and the metal, and thus lessen the time during which the reacting masses cover the electrode. Stirring will help to remove the reaction-products more rapidly. An increase in the hydrogen ion concentration will lessen the tendency for the formation of oxygen ions from the other ions, so that a potential difference higher than without the acid is required to bring about the same amount of dissociation into oxygen ions. Finally, a glance at the order of the anions in the list above reveals that this also is in accord with our theoretical notions: the ions which even with small current densities permanently affect the surface are hydroxylion, iodation, bromation, chloration, chromation—the first one of which is the oxygen ion itself, and the others are just the ions which may be expected to dissociate into free oxygen ions much more readily than the others further down the list.

The loss of the "permanent" effect which iron or nickel electrodes experience in all electrolytes after the current ceases to pass is in the nature of a discharge of a short-reputed cell: the "oxygen" spots act as the positive poles, and the uncovered spots (which were previously occupied by the reacting anions) act as the negative poles.

It has thus been shown that the general facts observed in these experiments are explained satisfactorily by the theory of anode actions first outlined. In conclusion a few special remarks should be made in anticipation of

possible objections raised to this theory or counter-claims made for other theories.

No special attempt was made to state in what particular form the oxygen obtained by the discharge of oxygen ions is present on the surface of iron or nickel anodes, that is, whether it is present as free oxygen or as oxide. To the writer there do not appear to be any facts which establish one view over the other (*Am. Chem. Journ.*, xli., 251). The assumption of a free oxygen film is perhaps a trifle simpler than the assumption of a formation of an oxide, but the possibility of the presence of an oxide has not been disproven even by the experiments of Mueller and Koenigsberger (*Phys. Zeit.*, vi., 847).

(NOTE.—These authors compare the reflecting power of two polished slabs of iron placed in sodium hydroxide solution. One of the slabs was "passivated" and then allowed to regain its normal state; and while it went through these changes its reflecting power was found to remain constant and the same as that of the slab which was not passivated. The fundamental error here is the assumption that the slab which was simply immersed was not acted upon; a slight electrolytic action undoubtedly took place between different spots of this slab, and the difference in the extent to which the slabs were affected is naturally much less conspicuous than the difference between a changed and an unchanged surface (and hence probably not observable).

Grave (*Zeit. Phys. Chem.*, lxvii., 513) has recently presented facts and arguments in support of Foerster's suggestions (*Abh. Bunsen Ges.*, No. 2) that the hydrogen in iron or nickel may be the catalyser to which they owe their activity, and hence when it is more or less completely absent these metals should be relatively inactive—passive. While it is a fact that hydrogen alloys with hydrogen or nickel, and that these alloys show a higher potential with higher per cents of hydrogen in them, yet these alloys really present only the same general relation which other alloys and other mixtures present. In the condensed form into which the hydrogen is probably compressed by the "surface effect" of the metal, the hydrogen itself would exhibit a potential as high or slightly higher perhaps than the alloys, and hence the potentials of the alloys thus appear to be below the potential of the "higher potential component"—a relation that is shown by all alloys. Furthermore, the activity of iron or nickel is also much greater with halide electrolytes than with others, such as sulphate electrolytes, even though hydrogen ions are equally absent in both electrolytes, and the theory of the catalytic influence of hydrogen upon these metals fails to account for this.

Possibly the best experimental evidence for a decision between this hydrogen catalysis theory and the theoretical views we have here advanced is the following.

A chromium anode that has become passive with reference to the formation of bivalent ions does not become active again to form trivalent ions, but does become active again to form chromation.

An iron anode that has been made passive with reference to the formation of bivalent ions does not become active again to form trivalent ions. However, when electrolysed in acetate or oxalate solutions the electrode becomes active again (that is, the metal dissolves again extensively) at potentials considerably below those (more noble!) at which it had ceased to be active before and at which it is usually passive in other electrolytes. The same thing is true of nickel (*Journ. Phys. Chem.*, xiv., 719; *Journ. Am. Chem. Soc.*, xxx., 1737).

In all three instances above the activity at the lower potential is due to a reaction which consumes oxygen and thus lays the metal surface bare. This is plainly the case in the formation of chromations. In the other examples the activity of the iron or nickel reappears when the potential is low enough to oxidise the acetion or oxalation, and when the oxygen is removed to oxidise these substances, then the metal surface is exposed and is subject to the attack of the anions,

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

M. EDMOND PERRIER ON CUVIER'S INFLUENCE ON
FRENCH SCIENCE.

At the Centenary Conference of 1914 organised by the *Revue Hebdomadaire*, M. Edmond Perrier, Director of the Natural History Museum, vividly described the great physiognomy of his predecessor at the Museum. At the conclusion of his lecture, M. Perrier said:—It is difficult to exercise over science a greater influence than that of George Cuvier. It may be considered as absolute up to 1860. The whole world was moved by his tragic recital of his revolutions of the globe, and enthusiastic over his wonderful reconstruction of animal forms that to-day have completely disappeared. Naturalists admired the magnificent arrangement of his classification, and his determinations of the age of terrestrial layers opened up new roads for geologists. Since then not only the order of the superposition of these layers has been determined, but the duration of time they took to form has also been measured, and was found to be immense. Cuvier's laws of the correlation of forms have since received many a rent; the four branches have become divided; it is no longer a question of the fixity of the species. Thus the whole of Cuvier's philosophy falls through; what remains of him is the revelation of the great variety of the organisation of unvertebrated animals; the resurrection of a long past of the earth; the rigorous order, the precise method introduced into all the branches of natural science; an unprecedented accumulation of new facts that might have led such a vast mind to higher conceptions if he had not voluntarily folded his wings. It is, above all, the example of a great life devoted to incessant labour for the greater value of science.

PSYCHOLOGY AND PSYCHIATRY.

In a lecture delivered at the Collège de France under the patronage of the Institut Général Psychologique, Dr. George Dumas, Professor at the Sorbonne, showed how useful the knowledge of normal psychology is to a clinician in order to make general symptomatology or special psychiatry. The lecturer then went on to study the services that psycho analysis and laboratory psychology may render to psychiatry. While making certain critical reserves on the first of these methods and on the systematic results that a contemporary school tries to draw from them, he showed the interest that may exist for the clinician in the analytical study of a delirium, and he indicated how far experimental psychology may serve psychiatry by giving more precision and objectivity to its measures, observations, and results.

INTENSITY OF HERTZIAN WAVES VARIES ACCORDING TO
THE WEATHER.

The intensity of the signals emitted by the posts of wireless telegraphy varies not only at different hours of the day, but also at different periods of the year. Extremely interesting researches on the variations of the intensity of radiotelegraphic signals have just been made by Prof. E. W. Marchand between Liverpool and Paris, and by Prof. Mossler in Germany. During a year, Prof. Mossler had measured both by day and night, by means of a detector and a galvanometer, the intensity of a current of reception in a station of wireless telegraphy situated at a distance of 425 kilometres towards the coast. He has remarked that during the day the intensity is not influenced by the height of the sun, and that this intensity remains constant for all the year, but that the characteristic maxima values are manifested during the night in autumn and in spring. In general Prof. Mossler observes that in summer one cannot reckon on a night reach of intensity much greater than of the day during the colder season. During the night very strong increases of intensity are re-

marked, which disappear rapidly. It would seem that they are to be attributed to the changes of ionisation of the higher atmosphere. In spite of very minute measurements no influence exercised by the brilliancy of the moon on the intensity of the signals has been observed. The observations of M. Marchand are not less curious. It is signals sent off by the Eiffel Tower at 10.45 o'clock in the morning and at 11.45 in the evening which have served him as a point of comparison. The result of these experiments shows that the maximum of variation of diurnal intensity of the signals during the same month is from 0.6 to 1.3, the average intensity being 1.1. On a fine clear night the signal has an intensity equal to 1.7 times that of the day signals. The meteorological state affects the intensity of the signals emitted and received. In Paris the rain always decreases the intensity of the reception. A wind blowing from the north-west at a speed of 6 metres per second has once lowered by one-half the normal intensity of reception. Cloudy weather is the most favourable for the transmission and reception of wireless telegraphy signals. If the sky is clear, or if there are only light clouds, the signals are weaker. The rain at the receiving station does not appear to have any great influence on the intensity of the Hertzian waves. A curious fact observed by M. Marchand and by the officers of the military wireless telegraphy is the strengthening of the intensity of the signal's immediately after sunset, which increase has sometimes amounted to 70 per cent. The intensity of the signals remained constant after the sudden strengthening. The explanation of these diverse phenomena still remains mysterious.

INVASION OF OYSTERS FROM PORTUGAL.

Portuguese oysters, which according to the opinion of zoologists do not even belong to the properly called species of oysters but to the *gryphæa* species, are threatening to invade the French oyster beds. M. Edmond Perrier, Director of the Natural History Museum, recalls to mind that the more robust Portuguese oysters have, in the region of Arcachon, supplanted the native oysters, which have a much finer taste. The Portuguese oysters are likewise attacking the Marennes oysters that are so highly appreciated. But it was thought that the danger was limited. It was not thought that the Southern *gryphæa* could become acclimatised on the Brittany coasts. Now such is not the case. The Portuguese oysters can very well live on the Brittany coasts, and they are threatening to gradually take the place of the oysters of Cancale that have a much better taste and are more appreciated. M. Dantan, who has made numerous studies on these molluscs, indicates, however, a means which will enable oyster cultivators to guard against the danger. This means is founded on the notable difference between the embryo of the ordinary oyster and of the Portuguese oyster. The embryo of the ordinary oyster develops inside the shell, whereas the embryo of the Portuguese, more undisciplined, comes out of the shell and goes and fixes itself on the collectors; that is to say, on the posts, fascines, tiles that are employed to collect the "naissin" or spawn. Indeed, the larva only develops on the surface. If, then, the collectors are driven down deeper, the embryos of the Portuguese oysters will no longer be able to live. The peril will thus be averted.

MOUNTAIN SICKNESS.

Some curious experiments on mountain sickness have been made by Dr. Guillemard, by the help of rabbits transported during the campaigns from the plain to the top of Mont Blanc, at an altitude of 4800 metres, and to the Marguerite hut, situated at the top of Mont Rose, at an altitude of 4560 metres. M. Armand Gautier remarks in the communication that he presents before the Academy, in the name of M. Guillemard, that the ureic nitrogen increases notably in the blood from the third day. The non-ureic nitrogen and the total nitrogen likewise increase. These phenomena seem to indicate that mountain sickness

is the result of a nitrogen intoxication. The urea, a toxic substance that should be eliminated by the kidneys, is retained by the organism. It is thus a veritable poisoning that occasions mountain sickness.

TRANSPARENCY OF LEAVES TO ULTRA VIOLET RAYS.

M. Dangeard has studied the transparency of leaves *vis à vis* to ultra-violet rays supplied by a mercury vapour lamp. He has observed, according to Prof. Mangin, that in a certain number of plants, particularly ferns, the leaves are much more transparent than glass for these rays. This is a somewhat remarkable result, if we consider that leaves have a complex structure. Begonia leaves and those of the China primrose have, on the contrary, the same transparency as glass for the ultra-violet radiations; moreover, there are other leaves that hardly let anything more pass than the extreme radiation of the visible spectrum more or less attenuated.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 5th, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Conduction of the Pulse Wave and the Measurement of Arterial Pressure." By Prof. L. HILL, F.R.S., J. MCQUEEN, and M. FLACK.

"Report of the Monte Rosa Expedition of 1911." By J. BARCROFT, F.R.S., M. CAMIS, C. G. MATHISON, F. ROBERTS, and J. H. RYFFEL.

I. Curves representing the equilibrium between oxygen and hæmoglobin were determined for *resting* individuals at Col d'Olen and the Capanna Margherita.

These and all others were capable of representation by the equation—

$$y/100 = \frac{Kx^n}{1 + Kx^n}$$

y = percentage saturation of hæmoglobin with oxygen.

x = oxygen pressure.

K = equilibrium constant of reaction.

n = average number of molecules of Hb assumed to be in an aggregate.

Notwithstanding a fall in the CO₂ pressure of the blood, no change in K could be detected, except as the mean of a large number of observations, when a slight fall in K , indicating decreased alkalinity of the blood, was apparent. The curves were determined in the presence of the existing alveolar CO₂ pressure.

II. The blood was investigated similarly after *exercise*, which usually consisted in climbing 1000 feet.

Climbs were made by the same individuals at—

1. Carlingford, co. Louth, from sea-level.

2. Col d'Olen, from 9000 feet.

A diminution in K invariably occurred. Climbing at a given rate the reduction in K was much greater at high altitudes. A given reduction in K involved much more rapid climbing at low altitudes. The change in K caused by *exercise*, whether at high or low altitudes, was entirely accounted for by the production of lactic acid.

Determinations of the hydrogen ion concentration in the blood of one have been made. These show a defined relation between C_H and K , so that the one may be calculated from the other.

"Some Notes on Soil Protozoa." (Part I.). By C. H. MARTIN and K. LEWIN.

It seems generally agreed that further examination of

the Amœbæ will necessitate splitting up the genus *Amœba*. The first and much needed step in this reform has already been taken by Chatton by the formation of the genus *Vahlkampffia* for the group of Limax Amœbæ. Whether it would not be better to put this genus, and all other Amœbæ which show a flagellate stage in their life-cycle apart from the gamete stage, into the group Proteomyxa seems to us an open question.

There can be no doubt that in this genus *Vahlkampffia* a number of quite definite species are included which can probably be best separated by minute differences in the behaviour of the nucleus during division. It will probably be found necessary in the same way to form another genus for the Lamellipodia group, which would again have to be broken up into a number of species in a similar manner.

The main purpose of this introductory paper is not the study of these Amœbæ from a specific point of view, so much as the proof which we hope to have brought of the existence of a relatively frequent trophic Protozoan fauna in certain soils, and the rough indication of possible methods of dealing with this fauna. How far this fauna, under certain conditions, exercises a deleterious influence on plant growth is a question for the agriculturist rather than the zoologist.

The startling success in the Lee Valley of the treatment of sick soils by partial sterilisation, introduced by Russell, would seem to present a very strong argument in favour of the view that these Protozoa do exercise an important influence on plant growth in these soils. We have been able to establish the occurrence of a trophic Protozoan fauna in certain field soils that we have examined, and on this question we hope to return in a future paper.

"Development of the Starfish, *Asterias rubens*, L." By J. F. GEMMILL.

"Floral Mechanism of *Welwitschia mirabilis* (Hook). By A. H. CHURCH, D.Sc.

CHEMICAL SOCIETY.

Ordinary Meeting, January 22, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 81).

15. "The Volatile Oil of *Cymbopogon coloratus* from Fiji." By ERNEST GOULDING and JOHN CAMPBELL EARL.

The essential oils derived from certain species of *Cymbopogon* are well known in commerce as "lemon-grass" and "citronella" oils. The former are derived mainly from *Cymbopogon flexuosus*, Stapf, and *C. citratus*, Stapf, and the latter from *C. nardus*, Rendle. The chief constituent of the lemon-grass oils is citral, the proportion of which is commonly between 70 and 80 per cent. The citronella oils, on the other hand, are characterised by the presence of considerable quantities of citronellaldehyde and geraniol, but contain very little or no citral.

In the course of a study of the various grass oils at the Imperial Institute, three oils have been encountered which have not hitherto been described, and exhibit characters very different from those of either the lemon-grass or citronella oils. One of these is furnished by the leaves of *Cymbopogon coloratus*, Stapf, and contains considerable quantities of citral and geraniol, but no citronellaldehyde.

In 1907, seeds of a lemon-grass were forwarded to Fiji from India, and the plant, since identified as *Cymbopogon coloratus*, Stapf, has been grown at Nasinu Experiment Station. It has been found by Knowles (*Bull.* No. 6, Dept. Agric., Fiji) that the fresh leaves of this grass, when distilled with steam, yield about 0.35 per cent of oil. Samples of oil distilled in Fiji were forwarded to the Imperial Institute in 1908 and 1909, and were subjected to a preliminary investigation (*Bull. Imp. Inst.*, 1912, x., 27).

Subsequently the oil was examined by Umney (*Perfumery and Essential Oil Record*, Dec., 1912, p. 317), who found it to contain 35 per cent of citral and 30 per cent of geraniol. A further sample of the oil has been received recently from Fiji, and has been submitted to examination, with the following results:—

The oil had D_{15}^{15} 0.912 and $[\alpha]_D$ at 24° , -10.31° , and contained 23 per cent of geraniol (estimated by the phthalic anhydride method). It was shaken successively with sodium carbonate, sodium hydrogen sulphite, and sodium hydroxide, and the residual oil was afterwards submitted to fractional distillation. The sodium carbonate solution extracted 0.75 per cent of the oil, consisting chiefly of acetic acid. The sodium hydrogen sulphite removed 34 per cent of aldehydes, but some of the aldehyde remained in the residual oil (see below). The aldehydic constituents had a pleasant lemon-like odour, and consisted almost entirely of citral. The treatment with sodium hydroxide extracted 0.75 per cent of phenolic substances, from which a small quantity of a white tasteless and odourless solid (m. p. 142° , decomp.) was isolated; the remainder consisted of a dark brown liquid with an odour recalling that of cloves, but the quantity was too small to admit of identification.

The residual oil still possessed a lemon-like odour, and an aldehyde estimation made by the sulphite method showed an absorption of 11 per cent. It furnished the following constants:— D_{15}^{15} 0.915; n_D^{22} $-12^\circ 29'$ (in 1-dcm. tube); ester value 42 (corresponding with 14.7 per cent of geranyl acetate and equivalent to 0.5 per cent in the original oil); saponification value after acetylation, 183 (corresponding with 43.4 per cent of alcohols, calculated as $C_{10}H_{18}O$). On distillation under 10–12 mm. pressure, the following fractions were obtained:—

Fraction.	Temperature.	Quantity, per cent.	D_{15}^{15} .	Optical rotation, in 1 dcm. tube.
A	Up to 80°	8.3	0.858	$-52^\circ 22'$
B	$80-105^\circ$	2.7	0.868	$38^\circ 35'$
C	$105-120^\circ$	27.1	0.902	$12^\circ 55'$
D	$120-130^\circ$	25.5	0.912	$6^\circ 4'$
E	$130-150^\circ$	13.7	0.937	$4^\circ 32'$
F	Residue and loss	22.7	—	—

Fraction A consisted largely of terpenes. A further quantity of terpenes was obtained by distilling some of the original oil on the water-bath under 15–20 mm. pressure. By this means a fraction amounting to 7.4 per cent of the original oil was obtained, which after repeated treatment with sodium and re-distillation had D_{15}^{15} 0.854, n_D^{20} $-62^\circ 39'$ (in 1-dcm. tube), and b. p. $168-173^\circ/760$ mm. The terpenes absorbed bromine to an extent corresponding with about 3 atoms per mol. $C_{10}H_{16}$, but the product could not be obtained in a crystalline state. It is probable that the terpenes were a mixture of *l*-limonene with one or more other terpenes, but the quantity of oil available was not sufficient to enable them to be identified.

Fraction B appeared to contain the constituents of A and C, and was not examined in detail.

Fraction C consisted chiefly of geraniol.

Fraction D contained more than 20 per cent of esters. After hydrolysis, it yielded a homogeneous crystalline diphenylurethane of geraniol (m. p. 82°). The readiness with which this derivative crystallised indicated the absence of citronelloldiphenylurethane.

Fraction E was readily soluble in less than three volumes of 70 per cent alcohol (indicating the absence of sesquiterpenes), and furnished geranioldiphenylurethane (m. p. 82°).

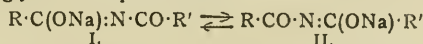
The residue F was dark brown and viscous. When submitted to distillation in steam, about one-fourth of it distilled over; the remainder probably consisted of resinous non-volatile polymerisation products formed during the distillation and fractionation of the oil.

The results of this investigation indicate that the oil of *Cymbopogon coloratus* has the following approximate composition:—

	Per cent.
Terpenes	7.5
Aldehydes, chiefly or entirely citral	40
Geraniol	23
Esters, chiefly geranyl acetate	10
Acetic acid	0.75
Phenols	0.75
Substances not identified	18

16. "The Hydrolysis of Mixed Secondary Amides by Alkalis." By ARTHUR WALSH TITHERLEY and LEONARD STUBBS.

A mixed secondary amide, $R \cdot CO \cdot NH \cdot CO \cdot R'$, under the influence of alkali, may conceivably suffer hydrolysis in two possible ways:—(1) Giving $R \cdot CO_2H$ and $R' \cdot CO \cdot NH_2$, or (2) giving $R \cdot CO \cdot NH_2$ and $R' \cdot CO_2H$. Direction (1) is followed exclusively when R' is an aromatic radicle and R is methyl, and this is attributed by the authors to steric influence. The mechanism of hydrolysis is probably one in which water-addition first takes place at the double link (C:N) of the tautomeric form of the secondary amide, yielding $R \cdot C(OH)_2 \cdot NH \cdot CO \cdot R'$, which then decomposes into the acid $R \cdot CO_2H$ and amide $R' \cdot CO \cdot NH_2$. Accordingly, in the equilibrium—



the rate of hydrolysis of I. is very much greater than that of II., and owing to continual disturbance of the equilibrium it is the only form the hydrolysis of which can be detected. Whilst the hydrolysis of diacetamide, acetylcarbamide, and acetobenzamide in the cold is complete within forty minutes, that of purely aromatic secondary amides under the same conditions requires about fifteen hours. The influence of spacial protection on the course of the hydrolysis is illustrated by the fact that benzo-*o*-toluamide, $Bz \cdot NH \cdot CO \cdot C_6H_4 \cdot CH_3$, yields benzoic acid and *o*-toluamide exclusively, whilst benzo-*p*-toluamide decomposes in both possible ways, yielding a mixture of benzoic and *p*-toluic acids, together with benzamide and *p*-toluamide. Although steric influence is potent in directing the course of hydrolysis of a mixed secondary amide, evidence is available that the affinity for water of the double link (C:N) is also a factor. In the hydrolysis of acetylcarbamide, which yields acetic acid and carbamide almost quantitatively, it is probable that the form $CH_3 \cdot C(ONa) : N \cdot CO \cdot NH_2$ only is involved. The two benzotoluamides above were obtained best by the condensation of the corresponding phenyl toluates and benzamide, and subsequent hydrolysis of the resulting toluoylbenzamidines, $NH : CPh \cdot NH \cdot CO \cdot C_6H_4 \cdot Me$.

17. "The Miscibility of Azobenzene and Azoxybenzene in the Solid State and the supposed Existence of a Stereoisomeride of Azobenzene." By HAROLD HARTLEY and JOHN McARTHUR STUART.

An examination of the freezing-point and melting-point curves of mixtures of azobenzene and azoxybenzene has shown that these substances form two series of mixed crystals with an eutectic temperature of 24.5° . The two mixed crystals deposited at this temperature contain respectively 45 per cent and 90 per cent of azoxybenzene molecules. The latter crystals are probably identical with the substance obtained by C. V. and R. A. Gortner (*Journ. Am. Chem. Soc.*, 1910, xxii., 1294) as a by-product in the preparation of azobenzene by the distillation of azoxybenzene with iron filings, and thought by them to be a stereoisomeride of azobenzene.

18. "The Influence of Colloids and Fine Suspensions on the Solubility of Gases in Water. Part IV. Solubility of Nitrous Oxide at Pressures Lower than Atmospheric." By ALEXANDER FINDLAY and OWEN RHYS HOWELL.

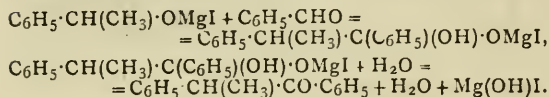
In continuance of previous work (*Trans.*, 1910, xxvii., 536), the solubility of nitrous oxide in water in the presence of ferric hydroxide, dextrin, starch, gelatin, egg-albumin, silicic acid, finely-divided silica, and finely-divided charcoal, has been determined at pressures lower

than atmospheric. The values obtained fit in well with those previously obtained at higher pressures, and the general type of solubility curve obtained is similar to that found in the case of carbon dioxide (*Trans.*, 1910, xcvi., 536; 1913, ciii., 636); that is to say, the solubility curves show a more or less pronounced minimum.

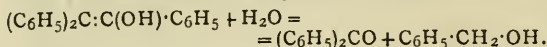
19. "The Action of Aldehydes on the Grignard Reagent." By JOSEPH MARSHALL.

It has been found that the addition of two molecular proportions of benzaldehyde to one molecular proportion of magnesium methyl iodide results in the formation of α -methyldeoxybenzoin, $C_6H_5 \cdot CH(CH_3) \cdot CO \cdot C_6H_5$.

The course of this reaction is indicated by the equations—



A similar result was obtained when benzaldehyde was allowed to react with magnesium dimethylcarbinyl iodide, in which case phenyl isopropyl ketone was isolated. When, however, two molecules of benzaldehyde were caused to react with one molecule of magnesium phenyl bromide, the products of the reaction were benzyl alcohol and benzophenone, instead of phenyldeoxybenzoin (triphenylvinyl alcohol), as was expected. This result may be explained by assuming that the triphenylvinyl alcohol is hydrolysed under the conditions of the experiment as follows:—



An analogous equation would explain the production of acetophenone when acetaldehyde is allowed to react with magnesium phenylmethylcarbinyl bromide.

An attempt was made to obtain phenylmethylacetaldehyde by allowing trioxymethylene to react with magnesium phenylmethylcarbinyl iodide, but the product of this reaction was phenylethyl iodide. Similar products were obtained when ethyl formate reacted with Grignard reagents, instead of the substituted acetic esters which were expected in these reactions.

20. "The Use of Sulphuryl Chloride in the Alkylation of Phenols." By WILHELMINA REBECCA SMYTH.

In view of the poisonous character of methyl sulphate, experiments have been carried out to ascertain whether it would be possible to use methyl alcohol and sulphuryl chloride in place of methyl sulphate as a methylating agent, and also whether other alcohols than methyl alcohol would react with phenols in the presence of sulphuryl chloride. The sulphuryl chloride was added to a slight excess of the alcohol, and when action was at an end the phenol was introduced. The mixture was allowed to remain for some time, and then treated gradually with a slight excess of alkali hydroxide. The ether formed was either extracted from the alkaline solution or removed by distillation in steam. In some cases before introducing the sulphuryl chloride the alcohol was treated with the calculated amount of metallic sodium, but this addition was not found to have any appreciable influence on the result. In other cases the sulphuryl chloride was cooled in a freezing mixture, and the alcohol slowly added, but here also the yields were not affected to any great extent.

The phenols treated in this way were phenol, catechol, carvacrol, and β -naphthol, the alcohols used being methyl and ethyl alcohol, and, in the case of the two last compounds, propyl alcohol. In all these cases alkylation occurs under the conditions just described, but, except in the case of β -naphthol, the ethers are only formed in small amounts. β -Naphthol yields about half the calculated amounts of the methyl, ethyl, and propyl ethers. Phenol gave from 15 to 25 per cent of anisole and phenetole, and catechol about 20 per cent of guaiacol, but no veratrole. Carvacrol gave only traces of the methyl, ethyl, and propyl ethers. In most cases practically the whole of the

unchanged phenol could be recovered from the alkaline solution.

Attempts to alkylate amino-compounds in a similar manner were not successful.

21. "The Colours produced on Mixing the Alkyl Nitrites with Substances containing Centres of Residual Affinity." By ERNEST MAGOWAN HARPER and ALEXANDER KILLIN MACBETH.

In view of the fact that many colour reactions have recently been obtained with the organic nitro-compounds, it appeared of interest to the authors to examine the alkyl nitrites. It was shown that these give colours with amino-compounds, ethylenic hydrocarbons, and substances containing bivalent sulphur. These colours are similar to those obtained with tetranitromethane when treated with the same substances. It is thought probable that the colour is due to an intermediate additive compound, the true final additive compound being colourless. Parallel to this is the Vorländer hypothesis, which deals with such cases to account for the two products when an acid reacts with an $\alpha\beta$ unsaturated ketone.

The final additive products of the nitrites and the primary, secondary, and tertiary amines have been isolated by Rây and Datta, Rây and Rakshit, and by Neogi, and the preparation of the corresponding compounds in case of the bivalent sulphur substances is being undertaken by the authors.

22. "The Progressive Bromination of Toluene." By JULIUS BEREND COHEN and PAVITRA KUMAR DUTT.

Cohen and Dakin (*Trans.*, 1901, lxxix., 1111) studied the progressive chlorination of toluene through successive stages from the hydrocarbon to the tetrachloro-derivatives. The results described by A. K. Miller (*Trans.*, 1892, lxi., 1023) on the bromination of *o*- and *p*-bromotoluene present certain differences in the quantity and character of the products when compared with those obtained by chlorination of the corresponding chlorotoluenes. The authors have therefore submitted the subject to a careful investigation, in which they have determined the character of all the bromine derivatives obtained by brominating the hydrocarbon and its mono- and di-bromo-derivatives.

The results of chlorination and bromination are given side by side in the following table for comparison, the principal product being placed first in each case, those occurring in smaller quantity standing next in order, whilst a trace is indicated by brackets.

Substance taken.	Bromination products.	Chlorination products.
Toluene.	Ortho, para, (meta).	Ortho, para.
<i>Monohalogen Compounds.</i>		
Ortho	2 : 5, 2 : 4	2 : 4, 2 : 3, 2 : 6, (2 : 5)
Meta	2 : 5, 3 : 4, (3 : 5)	2 : 5, 3 : 4
Para	2 : 4, 3 : 4	2 : 4, 3 : 4
<i>Dihalogen Compounds.</i>		
2 : 3	2 : 3 : 6, 2 : 3 : 5	2 : 3 : 4
2 : 4	2 : 4 : 5, (2 : 4 : 6)	2 : 4 : 5, 2 : 3 : 4, (2 : 4 : 6)
2 : 5	2 : 4 : 5, (2 : 3 : 6)	2 : 3 : 6, 2 : 4 : 5
2 : 6	2 : 3 : 6	2 : 3 : 6
3 : 4	2 : 4 : 5, (3 : 4 : 5)	2 : 4 : 5
3 : 5	2 : 3 : 5	2 : 3 : 5

Attention was directed to the difference in orienting effect produced by chlorination and bromination of the ortho-halogen derivatives, which is most marked in the case of the *o*-bromotoluene and in that of the 2 : 3- and 2 : 5-dihalogen derivatives.

23. "The Absorption Spectra of some Mercury Compounds." By CECIL REGINALD CRYMBLE.

It has been shown that groups attached to the mercury atom increase its absorptive power in the following order:—CN, Cl, $C_2H_3O_2$, $C_3H_5O_2$, Hg, Br, NO_2 , I, and that the absorption of the molecule depends on an interaction between the mercury atom and the attached groups.

Entrance of the mercury atom into complex haloid salts is accompanied by an increase in absorptive power. It is possible to determine the nature of the complex formed, and to follow its progressive dissociation on dilution. The complex MHgX_3 is formed quantitatively at decimolecular concentrations in alcohol. There is no spectroscopic evidence of the formation of any higher complex, such as M_2HgX_4 , in either alcohol or water.

The change in the properties of the mercury atom on passing from the dihaloid salt to the dialkyl compound has been compared with the corresponding change in the absorption spectra of these compounds.

24. "A New Phosphoric Ester obtained by the Aid of Yeast juice." (Preliminary Note). By ARTHUR HARDEN and ROBERT ROBISON.

In the preparation of hexosediphosphoric acid from lævulose and disodium hydrogen phosphate a second phosphoric acid derivative is also obtained. This is found in the filtrate after the separation of the diphosphate by treatment with lead acetate, and is precipitated on the addition of a solution of basic lead acetate. A portion of the new compound is also precipitated along with the lead hexosediphosphate, from which it can be separated by decomposing the salt with hydrogen sulphide, reprecipitating with lead acetate, and repeating these operations several times.

By decomposing the basic lead salt with hydrogen sulphide an aqueous solution of the acid itself may be prepared. It gives Seliwanoff's reaction, reduces Fehling's solution, and yields an osazone. It is strongly dextro-rotatory, the specific rotation being very much higher than that of hexosediphosphoric acid. When the solution is boiled phosphoric acid is liberated, and the rotatory power falls, whilst the reducing power is slightly increased.

The barium salt was obtained by neutralising the solution of the acid with baryta, filtering, and adding an equal volume of alcohol, whereupon the salt was precipitated as a white amorphous solid. It is readily soluble in both hot and cold water, differing in this respect markedly from barium hexosediphosphate. Various methods of purification have been employed, but the salt has not yet been obtained entirely free from nitrogenous impurities. The results of analyses, however, approximate fairly closely to those required for the barium salt of a hexosemonophosphoric acid, $\text{C}_6\text{H}_{11}\text{O}_6\text{PO}_3\text{Ba}$.

A similar compound is also obtained when dextrose is substituted for lævulose, but it has not yet been ascertained whether these two compounds are or are not identical. The investigation is being continued, and the relations of this substance to hexosediphosphoric acid and to the process of alcoholic fermentation are being studied.

SOCIETY OF CHEMICAL INDUSTRY. (LONDON SECTION).

Ordinary Meeting, February 2, 1914.

Prof. W. R. E. HODGKINSON in the Chair.

THE following papers were read and discussed:—

"Estimation of Zinc in Coinage Bronze by Volatilisation." By T. K. ROSE, A.R.S.M., D.Sc., Chemist and Assayer of the Mint.

This old process, discontinued about 1870, has recently been revived. It consists in heating 1 gm. of the alloy for two hours in a reducing atmosphere, at a temperature of 1375° , and weighing the residue. This sample is placed in a carbon crucible with a closely fitting lid, and 8 to 16 of these are embedded in charcoal in a graphite pot and heated in an injector furnace. Coinage bronze consists of copper 95, tin 4, zinc 1, and the loss of weight under the conditions used amounts to 1.2 or 1.3 per cent, about 0.03 per cent of zinc being retained in a residual metal. Proof assays consisting of portions of a trial plate of known

composition are included in each charge. The corrected results differ from each other by from 0 to 0.1 per cent, the average difference being about 0.02 or 0.03 per cent.

A few determinations of zinc in alloys containing various amounts of zinc up to 90 per cent have also been made, and found to agree with results obtained by the gravimetric and volumetric methods. As the amount of zinc is increased from 1 to 90 per cent the loss of copper rises from 0.2 to 0.4 per cent.

Sources of error are the presence of cadmium, oxygen, &c., which are reckoned as zinc, and occasionally black scales, probably sulphide of copper, adhering to the residue. Such assay pieces are rejected. Other errors are eliminated by the use of proofs. The advantage of the method is the saving of time, which is considerable, the personal time of the assayer being occupied for only three to five minutes for each determination.

"Nickel Tannates." By PURAN SINGH.

The author finds that by precipitating a solution of nickel hydroxide in ammonia salts with tannic acid solution, the nickel being in excess, a greenish white precipitate slowly changing into deep brown is produced. When dry this is blackish brown. This salt contains about 28 per cent of NiO, and may be $\text{Ni}_3(\text{C}_{14}\text{H}_7\text{O}_9)_2$. When the nickel hydroxide solution is added to a tannic acid solution, the latter being in excess, an almost white salt, which slowly acquires a greenish yellow tinge, is precipitated. This contains not more than about 10 per cent of NiO, and would appear to be the normal salt, $(\text{C}_{14}\text{H}_8\text{O}_9)\text{Ni}$.

The author states that though it has not been possible to obtain absolutely pure salts, it can be safely said upon the results obtained that only two theoretical salts have been proved.

"Oxygen and Metallic Antimony in Crude Antimony." By W. R. SCHOELLER, Ph.D.

Crude antimony, containing antimony 73.56 per cent and sulphur 22.45 per cent, was fused in a current of hydrogen sulphide; water was given off which was collected and weighed. 3.18 per cent of oxygen was thus found, and the crude after fusion assayed antimony 71.13 per cent, sulphur 27.56 per cent. Boiling tartaric acid solution dissolved four-fifths of the antimony combined to oxygen, which proved to be present as antimonious oxide. On repeatedly extracting the crude with hot strong hydrochloric acid, a residue assaying 97.17 per cent of antimony was obtained. The amount of metal present, as calculated from the results of the analysis, was 2.54 per cent.

The presence of antimonious oxide in crude antimony is due to absorption of oxygen by the molten sulphide, while the simultaneous presence of metallic antimony makes it more than probable that, contrary to the accepted view, antimonious oxide reacts upon the sulphide with formation of metal and sulphur dioxide, though the reaction takes place only to a limited extent.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Annual General Meeting, February 4, 1914.

THE following were elected the Officers and Council for the ensuing year:—

President—A. Chaston Chapman.

Past-Presidents—Leonard Archbutt, Edward J. Bevan, Bernard Dyer, Thomas Fairley, Otto Hehner, R. R. Tatlock, E. W. Voelcker, J. Augustus Voelcker.

Vice-Presidents—George Embrey, J. T. Hewitt, H. Droop Richmond.

Hon. Treasurer—Edward Hinks.

Hon. Secretaries—P. A. Ellis Richards, Rudolf Lessing.

Other Members of Council—E. M. Chaplin, J. H. Coste, G. H. Gemmell, Charles A. Keane, G. D. Lander, Thomas Macara, L. Myddelton Nash, Cecil Revis, Harry

Silvester, Arnold R. Tankard, Thomas Tickle, John White.

Ordinary Meeting, February 4, 1914.

Mr. CHASTON CHAPMAN, President, in the Chair.

Messrs. Alan Milsom Bailey, Arthur Leslie Barton, Thomas Sidney Haines, and Arthur George Abraham Miller were elected members of the Society.

Certificates were read for the first time in favour of Messrs. Robert Bickerstaffe, Chilterns, Wooburn Green, Bucks; Thomas Henry Byrom, 58, Hornsey Rise, Crouch End, London, N.; Sydney George Clifford, 3, Norman Villas, East Dulwich, S.E.; Donald Richard Frazer, Zeitzer Strasse 9, IV., Leipzig, Germany; and John McLaren, 7, Fauconberg Road, Chiswick, London, W.

Certificates were read for the second time in favour of Messrs. Rowland Holliday Ellis and Armand de Waele.

The following paper was read:—

"Iodometry of Arsenic, Copper, and Iron." By G. D. LANDER and J. J. GEAKE.

Cupric and ferric salts do not liberate iodine from potassium iodide in the presence of Rochelle salt and sodium bicarbonate. The quick volumetric process of Avery and Beans for arsenic copper mixtures is based on this fact. The authors have extended this method in the cases of copper and iron. Cuprous salts are oxidised by iodine in the presence of tartrate and bicarbonate, but in the case of ferrous salts this reversed action is incomplete.

NOTICES OF BOOKS.

Introduction to Modern Inorganic Chemistry. By J. W. MELLOR, D.Sc. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

THIS book is an introduction to the author's earlier work on inorganic chemistry, than which no better text book of its scope exists. The special aim of developing in the student a thoroughly scientific attitude of mind should be admirably fulfilled, and the use of the book should certainly inculcate habits of careful reflection and accurate deduction. Every device by which vivid impressions can be made upon the young student's mind is employed; such as variations of type, short sections dealing with one or two important points only, excellent diagrammatic illustrations, and the historical development of the subject is closely followed. Important discoveries and generalisations are usually associated with the name of some great chemist or physicist, and apposite quotations from classical scientific literature are frequently given. At the end of each chapter sets of questions are given; many of these are taken, in some cases with slight modifications, from public examination papers.

The Chemistry of Cattle Feeding and Dairying. By J. ALAN MURRAY, B.Sc. (Edin.). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

IN order to be able to use this book profitably the agricultural student should possess a sound knowledge of the rudiments of inorganic and organic chemistry, and should also be well grounded in the elements of mathematics. Given these qualifications he will be able to get a thoroughly scientific view of the problems of cattle feeding from the book. Much stress is laid upon quantitative work, and all practical advice as to feeding for milk production, fattening, &c., is based upon reliable statistics and calculations. The methods of graphic solution of problems connected with the compounding of foods are novel and interesting, and the chapter on the valuation of feeding stuffs and the table giving their average composition with the cost per food unit will be very useful to the farmer.

Elements of Water Bacteriology. By SAMUEL CATE PRESCOTT and CHARLES EDWARD AMORY WINSLOW. Third Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1913.

THIS book is intended for the use of students who, having some knowledge of general bacteriology, are ready for more advanced work in special branches. It is avowedly devoted chiefly to the consideration of American methods of investigation and interpretation, which however do not differ widely from those employed in England. The subject is treated in considerable detail, and an exceptionally complete bibliography is provided. A good deal of fresh matter will be found in the third edition, and a new chapter has been added dealing with the application of bacteriology to the sanitary study of shellfish, based largely upon the recent Report of the Committee of the Laboratory Section of the American Public Health Association.

The Analysis of Black Powder and Dynamite. By WALTER O. SNELLING and C. G. STORM. Washington: Government Printing Office. 1913.

THIS bulletin gives an outline of the methods of analysis employed in the laboratory of the Bureau of Mines in the examination of certain classes of explosives, e.g., ordinary dynamite, ammonia, gelatin, low-freezing and granular dynamites, and common grades of black gunpowder and black blasting powder. It will be a valuable guide for all who are interested in the analysis of explosives and their use in mining work, more especially as the details of the methods actually employed in the laboratories of explosives factories are often treated as trade secrets, while the descriptions of processes to be found in text-books are frequently insufficiently full.

The Prevention of Waste of Oil and Gas from Flowing Wells in California. By RALPH ARNOLD and V. R. GARFIAS. Washington: Government Printing Office. 1913.

IT is well known that the "coming in" of wells producing large quantities of oil and gas by natural flow is usually accompanied by great waste, and the Bureau of Mines has been conducting a series of investigations which aim at minimising these losses and also at preventing damage to productive oil and gas strata by the percolation of artesian waters into them. These investigations and their results are shortly discussed in this technical paper, both preventive and remedial measures being described. Special attention is paid to the methods of J. A. Pollard, which have been very successfully employed in the Buena Vista Hills.

Heavy Oil as Fuel for Internal Combustion Engines. By IRVING C. ALLEN. Washington: Government Printing Office. 1913.

THIS bulletin describes the results of the examination of the question of the practicability of more effectively burning the heavy asphaltum oils of the Pacific and Gulf Coasts of the United States. Although the results must be regarded as somewhat tentatively put forward, since the heavy oil-engine has not yet by any means attained its fullest development, it has been definitely proved that petroleum containing up to 20 per cent of asphaltum can be used for running the engines. The bulletin contains specifications of the fuels and lubricants which may be used for internal combustion engines of the heavy oil type, and epitomises the advantages of such engines over steam and explosion engines for marine purposes.

Brief Biography and Popular Account of the Unparalleled Discoveries of T. F. See, A.M., Lt.M., Sc.M. (Misson); A.M., Ph.D. (Berol). By W. L. WEBB. Lynn, Mass.: Thos. P. Nichols and Son. 1913.

PROF. SEE, who has done some remarkable work the value of which has been fully recognised on all sides, has found in Mr. W. L. Webb an enthusiastic biographer, who

expresses himself occasionally in somewhat extravagant language. The incidents of Prof. See's early life and of his academical career are reproduced in great detail, and the book also contains a full account of his work in astronomy and of the foundation of the new sciences, Cosmogony and Geogony. The author describes him as occupying easily the first place among living natural philosophers since the death of Poincaré and of Sir George Darwin in 1912, and regards his talents and achievements as quite unprecedented in the world's history. The book contains full reports of many of the addresses and lectures delivered by Prof. See and is copiously illustrated.

La Soudure Autogène. ("Autogeneous Welding"). Paris: Librairie du Mois Scientifique et Industriel. 1913. (2 fr. 75).

METHODS of autogeneous welding have come much to the fore in recent years, and the subject is one of which all up-to-date engineers and mechanics should have some knowledge. There are many different methods of welding to choose from, and this book is intended to provide a means of ascertaining which is preferable in given circumstances. The principles of autogeneous welding are explained in it clearly and impartially, and the advantages and disadvantages of the different processes are fully pointed out. In addition practical details concerning the handling of the necessary apparatus are also given, and some information as to the cost of different processes.

Notions Fondamentales de Chimie Organique. ("Fundamental Theories of Organic Chemistry"). By CHARLES MOUREU. Fourth Edition. Paris: Gauthier-Villars. 1913.

IN this book a summary is given of the main theories of organic chemistry, and matters of detail are omitted except in so far as the consideration of them is necessary for the understanding of the theoretical conceptions. The fourth edition has been carefully revised, and additional space is given in it to catalytic reactions and to methods of synthesis based upon the use of organo-metallic compounds. Important reactions brought about by light and the ultra-violet rays are described, and in stereo-chemistry active compounds containing no asymmetrical atoms are discussed, and also the transformation of an active substance into its optical antipode.

Die Quantitativen Untersuchungsmethoden des Molybdäns, Vanadiums, und Wolframs. ("Quantitative Methods of Estimating Molybdenum, Vanadium, and Tungsten"). By Dr. HANS MENNICKE. Berlin: M. Krayn. 1913. (Mk. 8).

THE metals molybdenum, vanadium, and tungsten and their alloys and compounds have recently greatly increased in importance from an industrial point of view, and a book devoted exclusively to the consideration of methods of detecting, estimating, and separating them is sure of a good reception. The author of this book has collected his material from all sources and has carefully sifted it. In many cases he has personally tested the methods described, and notes are frequently added as to the accuracy or rapidity of a method, while slight modifications are sometimes suggested. References are given to original literature, and all experimental details are fully stated. Most of the methods described are gravimetric or volumetric, very little space being given to colorimetric or electrolytic methods which cannot be relied upon for accuracy, and hence are not usually employed.

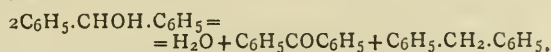
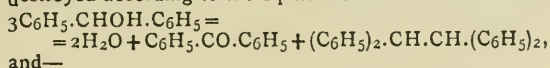
Physical Society.—The first Guthrie Lecture will be delivered by Prof. R. W. Wood (of Johns Hopkins University, Baltimore), at the Imperial College of Science, Imperial Institute Road, South Kensington), on Friday, February 27, 1914, at 8.30 p.m. The subject of the lecture will be "Radiation of Gas Molecules Excited by Light."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clvii., No. 26, December 29, 1913.

Contributions to the Study of Benzhydrol. Preparation of Symmetrical Tetraphenylethane.—Pau Sabatier and M. Murat.—Diphenylcarbinol or benzhydrol, $\text{C}_6\text{H}_5\cdot\text{CHOH}\cdot\text{C}_6\text{H}_5$, can be obtained by reducing with sodium benzophenone dissolved in amyl alcohol, but attempts to prepare it by Grignard's reaction failed, the chief products being benzophenone, diphenylmethane, and symmetrical tetraphenylmethane. Tetraphenylethane can be obtained by the hydrogenation of benzophenone, benzhydrol, or its oxide. The hydrogenation of tetraphenylethane gives diphenylmethane and dicyclohexylmethane. Thus the destruction of the organomagnesium complex gives, instead of benzhydrol, a product of dehydrogenation, benzophenone, and at the same time the products of hydrogenation diphenylmethane and symmetrical tetraphenylethane. The reaction of benzophenone with some mixed aliphatic organomagnesium compounds is analogous. Apparently the nascent benzhydrol is destroyed according to the equations:—



Transformations of Chromic Fluosilicate. Fluopentaquochromic Fluosilicate.—A. Recoura.—Chromic fluosilicate, $(\text{SiF}_4)_3\text{Cr}_2\text{F}_6$, unlike the ferric salt, does exist, although in solution it is very rapidly converted into a green compound of formula $\text{SiF}_6\cdot\text{CrF}_5\cdot\text{H}_2\text{O}$. This substance is fluopentaquochromic fluosilicate, corresponding to Jørgensen's two fluosilicates. It is perfectly stable in the desiccator, even *in vacuo*, but loses silicon fluoride when exposed to air, at first rapidly and then gradually more slowly, being finally transformed into a green fluoride of chromium of composition $\text{Cr}_2\text{F}_6\cdot 7\text{H}_2\text{O}$.

Determination of Chromium by Oxidation in Alkaline Medium.—F. Bourion and A. Sénéchal.—To determine chromium, soda is added to the chromic salt until the oxide formed is just dissolved and the solution is oxidised by means of hydrogen peroxide, the excess of which is decomposed by heating. The chromic acid is then reduced in a sulphuric solution by a known quantity of ferrous sulphate, the excess of which is determined with potassium permanganate. The chromium is obtained by difference. The authors find that this method gives accurate results when the chromium is alone or accompanied by iron. The destruction of the excess of hydrogen peroxide is greatly facilitated by the presence of sodium sulphate. The method fails in presence of nickel, cobalt, and manganese.

Vol. clviii., No. 1, January 5, 1914.

Ferrous Sulphate and its Hydrates.—R. de Forcrand.—Ordinary green vitriol always retains a certain amount of mother-liquor, which may be removed by powdering it and pressing between absorbent paper. Thus a powder of composition exactly corresponding to $\text{SO}_4\text{Fe}\cdot 7\text{H}_2\text{O}$ may be obtained. It is absolutely stable in air at 15° , and does not either oxidise, effloresce, or deliquesce. When kept over sulphuric acid at the ordinary temperature and pressure for three days it yields the tetrahydrate. The dehydration of either of these hydrates at 100° gives the monohydrate. The preparation of the anhydrous salt is much more difficult, and the author believes that it has never yet been obtained in a pure state.

The monohydrate begins to lose water at 180° in a current of dry hydrogen, but the process is very slow. To effect complete dehydration within a reasonable time the temperature must be raised to 250° , but at that temperature a little basic salt is formed. The author has obtained the following values for the heats of solution at 13.5° :— $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, -4.323 cal.; $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$, $+1.599$ cal.; $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, $+7.538$ cal.; FeSO_4 , $+14.901$ cal.

Researches on Cadmium.—Manuel Veres.—When a fifth of its weight of cadmium sulphate is added to fused ammonium bisulphate at 300° a deposit of $2\text{CdSO}_4 \cdot \text{Am}_2\text{SO}_4$ is obtained. This salt, which has not been described before, is very soluble in water, and when its solution is slowly evaporated monoclinic crystals of $\text{CdSO}_4 \cdot \text{Am}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ separate. $2\text{Cd}_2\text{SO}_4 \cdot \text{Am}_2\text{SO}_4$ is attacked by concentrated H_2SO_4 at 100° , anhydrous CdSO_4 being left as the residue.

Bulletin de la Société Chimique de France.

Vol. xiii.-xiv., No. 24, 1913.

Preparation of Allyl Alcohol.—A. Kochler.—To prepare allyl alcohol heat 100 grms. of glycerin for one hour with 80 grms. of formic acid, and separate by distillation into three fractions:—(i.) The liquid coming over below 200° ; (ii.) that passing over between 200° and 250 – 260° ; (iii.) the residue. Determine the saponification index of (ii.). Add twice the corresponding quantity of solid potash, boil for an hour, and allow to cool. Decant off the upper layer, and dry by boiling with half its weight of dry potassium carbonate for four hours. The yield of allyl alcohol amounts to 32 per cent. Monoformine is the intermediate product.

Decomposition of Benzylidene-phenylisoxazolone by Phenyl Hydrazine.—André Meyer.—When equimolecular quantities of benzylidene-phenylisoxazolone and phenylhydrazine are boiled with alcohol the isoxazolone dissolves, and on dilution with water a colourless compound is precipitated. This is benzylidene phenylhydrazine. The mother-liquor yields on evaporation a small quantity of a substance the properties of which recall those of the phenylisoxazolone, and also uncrystallisable substances which have not been identified. Thus phenylhydrazine splits up the molecule at the double bond. Hydroxylamine and bases capable of combining with aldehydes and ketones behave similarly.

Berichte der Deutschen Chemischen Gesellschaft.

Vol. xlv., No. 16, 1913.

Methylation of Metals by Action of Aluminium Carbide on Dissolved Salts.—Siegfried Hilpert and Martin Ditmar.—When aluminium carbide is introduced into a hydrochloric acid solution of sublimate, mercury methyl chloride is formed; in a neutral or faintly acid solution mercury dimethyl results. Bismuth trimethyl can be synthesised in the same way. Tin salts can also be methylated by means of aluminium carbide, and the formation of the methyl tin derivatives, which are readily detected by their strong characteristic smell, can be employed as a test for the metal. Probably like water or hydrochloric acid mercury chloride can bring about the decomposition of aluminium carbide. The negative chlorine combines with the aluminium, while the monovalent radicle HgCl , with three of the hydrogen atoms coming from the water or the hydrochloric acid, combines with the carbon.

MISCELLANEOUS.

Royal Institution.—On Saturday next, February 28, at 3 o'clock, Prof. Sir J. J. Thomson begins a course of six lectures on "Recent Discoveries in Physical Science." On Tuesday, March 3, Prof. Sir J. H. Biles delivers the first

of three lectures on "Modern Ships—(1) Smooth Water Sailing; (2) Ocean Travel; (3) The War Navy." On Thursday, March 5, Prof. C. F. Jenkin begins a course of three lectures on "Heat and Cold." The Friday Evening Discourse on February 27 will be delivered by Prof. W. A. Bone on "Surface Combustion," and on March 6 by Canon Hannay (George A. Birmingham), on "The Stage Irishman."

Anglo-American Exposition (May to October), 1914.—The Photography Committee of the Anglo American Exposition, 1914, is anxious to make this Section as widely known as possible—especially amongst manufacturers. The Exposition will afford a unique opportunity of bringing British industries to the notice of visitors from all parts of the world. From the communications that have been received from the United States Office there appears to be no doubt that the Exposition will be warmly supported by American exhibitors and the Government of the United States, and will be visited by large numbers of Americans. It is the desire of the British Committee that the Photography Section shall be the most extensive ever brought together and worthy of the British Empire. *Liberal Arts Sub-committee (Photography)*—E. Sanger-Shepherd (Chairman); Chapman Jones, F.I.C. (Vice-Chairman); Sir William Abney, K.C.B., F.R.S.; Charles F. Butler, A.R.C.Sc., F.R.P.S., F.R.A.S.; F. Martin Duncan, F.R.M.S., F.R.P.S.; Dr. R. T. Jupp, M.B., B.Sc., F.R.C.S.; Prof. R. Meldola, D.Sc., LL.D., F.R.S.; Frank F. Renwick, A.C.G.I., F.C.S., F.R.P.S.; Sir Philip Watts, K.C.B., LL.D., F.R.S., D.Sc.; Sir Henry Truman Wood; Sir J. Benjamin Stone, J.P., F.S.A., F.S.S.; Charles Urban, F.Z.S. *Classification*—Raw materials, instruments, and apparatus of photography; materials for photographic studies; positive and negative photography on glass, paper, woodstuffs, enamel, &c.; photogravure, photo-colotypes, photo-lithography, stereoscopic proofs; photographic enlargements and reductions; colour photography; natural and artificial colour printing; cinematography, apparatus, and processes.

MEETINGS FOR THE WEEK.

- MONDAY, 23rd.—Royal Society of Arts, 8. (Cantor Lecture). "Artistic Lithography," by Joseph Pennell.
- TUESDAY, 24th.—Royal Institution, 3. "Animals and Plants under Domestication," by Prof. W. Bateson, F.R.S., &c.
- WEDNESDAY, 25th.—Royal Society of Arts, 8. "Rural Housing," by T. Brice Phillips.
- THURSDAY, 26th.—Royal Institution, 3. "Hamlet in Legend and Drama," by Prof. I. Gollancz, Litt.D.
- Royal Society. "Diffraction of Light by Spheres of Small Relative Index," by Lord Rayleigh.
- Studies of the Properties Operative in Solutions—XXXI., Sulphonic Acids and Sulphuric Acid as Hydrolytic Agents—a Discussion of the Constitution of Sulphuric and other Polybasic Acids and of the Nature of Acids; XXXII., The Influence of Sulphonates on the Hydrolytic Activity of Sulphonic Acids—a Contribution to the Discussion on the Influence of Neutral Salts," by H. E. Armstrong and F. P. Worley. "Morphological Studies of Benzene Derivatives—V., The Correlation of Crystalline Form with Molecular Structure, a Verification of the Barlow-Pope Conception of 'Valency Volume,'" by H. E. Armstrong, R. T. Colgate, and E. H. Rodd. "Magnetic Properties of Iron when shielded from the Earth's Magnetism," by E. Wilson. "Occurrence of Ozone in the Upper Atmosphere," by J. N. Pring. "Meteoric Iron from Winburg, Orange Free State," and "Electrification produced during the Raising of a Cloud of Dust," by W. A. D. Rudge. "Electrical Ignition of Gaseous Mixtures," by W. M. Thornton.
- FRIDAY, 27th.—Royal Institution, 9. "Surface Combustion," by Prof. W. A. Bone, F.R.S.
- Physical, 8.30. (At the Imperial College of Science, South Kensington). "Radiation of Gas Molecules Excited by Light," by Prof. R. W. Wood.
- Swedenborg Society, 8.15. (At 1, Bloomsbury Street). "The Body and the Soul in Swedenborg's Philosophy," by L. de Beaumont-Klein, D.Sc.
- SATURDAY, 28th.—Royal Institution, 3. "Recent Discoveries in Physical Science," by Prof. Sir J. J. Thomson O.M., F.R.S.

THE CHEMICAL NEWS

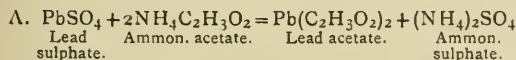
VOL. CIX., No. 2831.

NOTES ON THE EFFECT OF TUNGSTEN ON THE AMMONIUM-MOLYBDATE ASSAY FOR LEAD.

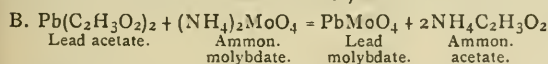
By HERBERT LAVERS.

At a previous meeting of the Broken Hill Branch of the Institute the writer reported the occurrence of two minerals in the sulphide zone of Block 14 Mine, both of them new to Broken Hill. They were wolfram and scheelite. The former—wolfram—a tungstate of iron and manganese, gave on assay 42 per cent tungstic acid. The latter—scheelite—a tungstate of lime, gave 35 per cent tungstic acid. Both these samples contained zinc and lead sulphides, and clean specimens of wolfram gave 64 per cent WO_3 ; scheelite gave 70 per cent WO_3 .

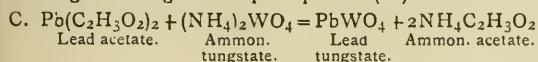
An estimation of the lead in these samples revealed the fact that the presence of tungsten in the ore seriously interfered with the ammonium-molybdate assay for lead, giving low results according to the amount of tungsten present in the ore. The sample under review, when assayed under ordinary conditions, gave a negative value for lead, but on removal of the tungsten showed 9.8 per cent Pb. The reason for this interference is shown on an examination of the reactions which occur in the assay. The ore is reduced with suitable acids, and the lead obtained in the form of sulphate, which is dissolved in ammonium acetate, thus:—



The lead acetate thus formed is now titrated with a standard solution of ammonium molybdate as follows:—



The above reactions take place under ordinary conditions, but when the ore contains tungsten, this is converted into the trioxide by the action of the acids, and during solution by ammonium acetate it readily combines with the lead, forming lead tungstate as per equation (C).—



So that if sufficient tungsten be present in the ore to combine with all the lead present, the addition of the standard solution gives negative results.

It therefore becomes necessary to remove the tungsten before proceeding with the lead assay, and this is done in the following way:—

The ore is digested in 10 cc. HCl , 10 cc. HNO_3 added, and evaporated to small bulk. This is taken up with water, boiled, allowed to settle, and filtered. By this means the tungsten is converted into tungstic acid, and removed with the silica. To the filtrate is added H_2SO_4 taken to white fumes (this is important, otherwise gives 0.2 high in 14 per cent lead), and the assay proceeded with in the usual manner.

The reaction occurring in equation (C) suggested a rapid volumetric method for the estimation of tungsten.

The tungstic acid obtained on the filter-paper in the previous operation is dissolved in ammonium hydroxide, neutralised with acetic acid, and an excess of standardised solution of lead acetate added. This combines with the WO_3 to form lead tungstate as per equation (C). The excess of lead acetate solution is now titrated with ammonium molybdate solution, as in the ordinary lead assay,

and shown by equation (B). From the formula PbWO_4 the factor for tungstic acid, WO_3 , can be obtained.

The presence of tungstic acid has no effect on the zinc assay. A laboratory experiment in flotation was carried out on some sulphide ore containing scheelite in order to see if this method could be used in separation. The following results were obtained.

	Lead.	Silver.	Zinc.	WO_3 .
No. 1 concentrate ..	52.4	23.4	13.2	—
Residue	2.8	15.6	1.0	20.4
No. 2 concentrate ..	53.6	26.2	12.6	—
Residue	3.5	14.2	1.0	17.4

Note the high silver in the residue, which latter readily lends itself to further concentration by tabling.

The above has a local interest from the fact that lead concentrate made from a parcel of Block 14 ore showed the presence of 5.5 per cent WO_3 . The concentrate contained 63 per cent lead (approx.), and the assay value shown by buyer and seller differed by upwards of 3 per cent. The umpire, who evidently recognised and removed the tungsten, agreed with the higher of the two assays.

The method shown above for the elimination of the tungsten in the determination of the lead was embodied in an agreement for the purchase of crude ore from Block 14 Mine, and has also been adopted in the lead assay for the purchase of certain lead concentrates.—*Australasian Institute of Mining Engineers*, 1913, No. 10.

THE APPLICATION OF DIPHENYLCARBAZIDE AS INDICATOR IN THE TITRATION OF IRON WITH DICHROMATE.

By O. L. BARNEBEY and S. R. WILSON.

BRANDT (*Zeit. Anal. Chem.*, xlv., 95, published, in 1906, a method using diphenylcarbazide ("Beistein," iv., 671), called by him "diphenylcarbohydrazide," as an "inside indicator" for the titration of iron. Shortly after the publication of the article one of us tried the method as outlined by Brandt and by following his directions minutely could not obtain concordant results. A detailed study, however, developed an interesting and valuable modification of this method and likewise an application for the analysis of ores.

In 1900, Cazeneuve (*Bull. Soc. Chim.*, xxiii., 592, 701, 769) pointed out the fact that diphenylcarbazide could be used to detect extremely small quantities of chromic acid, giving the sensitiveness as 1 : 1,000,000. Brandt carries the work further and uses this substance as an indicator for the titration of iron. He states that large amounts of hydrochloric acid and also manganese sulphate solution containing phosphoric acid must be present to prevent too rapid destruction of the indicator. His conditions for titration are—0.2 to 0.7 gm. of iron, 60 to 80 cc. dilute hydrochloric acid (sp. gr. 1.12), 100 cc. manganese sulphate solution (containing 6 kg. manganese sulphate), 33 litres dilute sulphuric acid (1 : 3), 3 litres phosphoric acid (sp. gr. 1.7) diluted to 60 litres,—diluted to a total volume of 1½ litres, and 5 cc. of a 0.1 per cent solution of indicator added. Smaller amounts than 0.2 gm. of iron may be titrated by slightly modifying the conditions.

The colour changes involved are very marked. The first drop of dichromate added gives a pink or red tinge, which becomes deep red as the titration proceeds. This colour gradually changes to lavender, which seems to be caused by the complementary nature of the red compound and trivalent chromium. The lavender fades out and finally the addition of one drop of the dichromate gives a sharp change to the clear green colour of chromic chloride.

Experimental.

The indicator was prepared by heating 20 grms. of urea with 200 cc. of phenylhydrazine, gradually raising the temperature from 150 to 170° for about four hours. The resulting product was dissolved in hot alcohol, re-crystallising by cooling, filtered, and washed with cold alcohol. The re-crystallisation was repeated three times. The crystalline product was nearly pure white, but had a tendency to gradually become pink when exposed to the air for some time. The melting-point was 163.5° ("Beilstein," *loc. cit.*). The colour tests outlined by Skinner and Ruheman (*Journ. Chem. Soc.*, liii., 551) were also tried with positive results. Solution was effected by dissolving the indicator in strong acetic acid and diluting to an appropriate volume. One gram. per litre is convenient.

A manganese sulphate solution was prepared by using the following proportions:—200 grms. of manganese sulphate, 1100 cc. of dilute sulphuric acid containing one part of acid (sp. gr. 1.84) and three of water, 100 cc. of phosphoric acid (sp. gr. 1.70) diluted to two litres.

Titration 25 cc. portions of a 0.1 N solution of ferrous iron and varying amounts of indicator, manganese sulphate solution, and acid with 0.1 N dichromate solution required from 25.60 to 28.00 cc. of the latter. Using constant amounts of the iron, manganese sulphate solution, and acid, having the indicator only as variable, gave results of the same order. However, by using constant amounts of indicator, variable amounts of manganese sulphate solution, variable amounts of acid, and constant amounts of ferrous iron in a series of determinations practically the same quantity of dichromate was required in each titration.

Series I. of the table is a series of "blanks" obtained with an indicator solution (about 0.17 per cent indicator) without the presence of ferrous iron, and Series II. in the presence of a constant quantity of iron in the ferrous state. Series I. was obtained as follows:—To about 300 to 400 cc. of water 10 cc. of strong hydrochloric acid, 10 cc. of manganese sulphate solution, and a measured amount of indicator solution are added followed by 3 cc. of 10 per cent ferric chloride solution, and the indicator titrated slowly with tenth normal dichromate, agitating very vigorously after the addition of each drop. The disappearance of the red and appearance of a pale green tint marks the end point. From three to five minutes must be taken for the titration to avoid over-running the end. Series II. varies from Series I. only in the use of constant quantities of 0.1 N ferrous iron and the use of 0.1667 N dichromate solution.

A glance at these figures shows at once that the indicator itself is the cause for the variable results, the larger the amount of indicator used the more dichromate is necessary to complete the titration. A regular increase in quantity of dichromate is noticed in both series as the amount of indicator becomes larger. In Series II. the value of 6 cc. of the oxidising agent is closely approached in each titration if in each case the dichromate equivalent to the amount of indicator used is subtracted; thus, 5 cc. of the indicator required 0.86 cc. of dichromate with no ferrous iron present. Hence, if the value of this blank is subtracted from the value found with 10 cc. of ferrous iron and 5 cc. of indicator present, 6 cc. in one case and 6.04 cc. in the other is found to be the actual volume of oxidising solution required. Brandt says nothing about this factor; in fact he even states that the quantity of indicator may be doubled and still have no appreciable effect on the titration. Although the titrations were made in a smaller volume than those of Brandt, yet using the dilution he recommends his results could not be confirmed. The work above suggested a direct ratio existing between oxidising agent and indicator.

To test this ratio more rigidly an exactly 0.1 per cent solution of the indicator was prepared and 10 cc. of this solution titrated with a solution of dichromate containing 0.00438 gram. per cc., the latter being standardised against

SERIES I.

HCl.	Indicator.	Manganese solution.	FeCl ₃ .	0.1 N K ₂ Cr ₂ O ₇ .
Cc.	Cc.	Cc.	Cc.	Cc.
10	0.5	10	3	0.14
10	0.5	10	3	0.18
10	1.0	10	3	0.30
10	1.0	10	3	0.32
10	2.0	10	3	0.60
10	2.0	10	3	0.60
10	3.0	10	3	0.92
10	3.0	10	3	0.96
10	4.0	10	3	1.22
10	4.0	10	3	1.20
10	5.0	10	3	1.42
10	5.0	10	3	1.42
10	10.0	10	3	2.76
10	10.0	10	3	2.74
10	15.0	10	3	4.18
10	15.0	10	3	4.26

SERIES II.

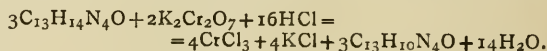
(10 cc. of ferrous iron solution are equivalent to 6 cc. of dichromate solution).

0.1 N ferrous iron solution.	HCl.	Manganese solution.	Indicator.	FeCl ₃ .	0.1667 N K ₂ Cr ₂ O ₇ .
Cc.	Cc.	Cc.	Cc.	Cc.	Cc.
10	10	10	2	3	6.36
10	10	10	2	3	6.36
10	10	10	5	3	6.90
10	10	10	5	3	6.86
10	10	10	10	3	7.62
10	10	10	10	3	7.66
10	10	10	15	3	8.46
10	10	10	15	3	8.48
None	10	10	5	3	0.86

pure ferrous ammonium sulphate, using ferricyanide as indicator on a spot plate. One and eight-tenths cc. of the dichromate, or 0.0079 gram., were required for the titration. Using the proportion:—

Wt. of indicator.	Weight of dichromate.	Mol. wt. of indicator.	Mol. wt. of dichromate.
0.01	0.0079	x	294
$x = 370$			

However, the molecular weight of the indicator is 242; hence, the number of molecules reacting would be $370 \div 242 = 1.5$ for each molecule of dichromate, and the reaction would probably be—



This equation is advanced for the lack of a better one at the present time. On the basis of three molecules of indicator being equivalent to two molecules of dichromate the following ratio holds:—3 mols. $\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$ (726) : 2 mols. $\text{K}_2\text{Cr}_2\text{O}_7$ (588) :: Wt. of indicator : Wt. of dichromate. Weighing out exactly 0.01 gram. of indicator and using 0.02 N potassium dichromate solution required 8.24 cc., or 0.00807 gram. of the latter. Theoretically calculating 0.01 gram. of the indicator according to the above proportion gives 0.00809 gram. of dichromate. In all likelihood side reactions may occur under some conditions of titration, in which cases the agreement may not be so close to the theoretical.

This process was repeated, using permanganate instead of dichromate, and the theoretical ratio of five molecules of indicator to four of KMnO_4 verified by experiment. A standard solution of chlorine water was likewise used and the ratio of two molecules of Cl_2 to one of indicator found to exist.

Analysis of Iron Ores.

We find that this method of determining iron can be readily applied to the analysis of iron ores. A 0.5 gm. (larger if the ore is of low grade) sample is weighed into a number two beaker. Pour over the sample 15 to 33 cc. of hydrochloric acid (sp. gr. 1.2), heat just below boiling, adding sufficient stannous chloride (200 grms. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 150 cc. of hydrochloric acid, sp. gr. 1.20, per litre) to reduce most of the iron as it dissolves yet leaving a distinct yellow tinge in the solution when the solvent action has ceased.

If a dark residue remains, filter, wash free from hydrochloric acid, and ignite the filter paper in a platinum crucible. Add a small quantity of sodium carbonate to ash, heat to quiet fusion. Cool, place crucible in a small beaker, and dissolve the melt in a small portion of boiling water. Add solution and precipitate, if any, to the hydrochloric acid extraction.

Heat the solution to boiling, wash off the cover and the sides of the beaker with a small portion of water (the volume should not be over 30 to 40 cc.), and add stannous chloride drop by drop to the hot solution until one drop will give a colourless solution, then add one drop in excess. (If a larger excess of stannous chloride has been added, add potassium permanganate until a permanent yellow colour appears, then reduce as above.) Transfer to a litre beaker, dilute to about 500 or 600 cc., add 30 cc. of mercuric chloride (saturated solution), stir vigorously for a moment, then add 20 cc. of manganese sulphate solution followed by 10 cc. of concentrated hydrochloric acid and an exact volume (2 to 3 cc.) of the indicator. Titrate with standard dichromate. The first few drops added will cause an intense red colour to appear. This colour changes to a purple as the titration proceeds, and as the end-point is approached it gradually fades, finally giving the sharp change to the chromic chloride. This gradual change minimises the danger of overtitration and allows the titration to proceed rapidly. The burette reading is now taken. The dichromate value of the indicator is obtained by titrating the same volume of the indicator as was employed previously under the same conditions as those of an actual analysis, except that 3 cc. of a 5 per cent solution of ferric chloride are added preceding titration. The blank titration must be performed very slowly to avoid overtitration. Another method used to check the reducing value of the indicator solutions consisted in starting with a definite amount of ferrous iron in solution, adding the usual amounts of manganese sulphate, acid, and 2 cc. of indicator, then titrating. Utilising the same amounts of ferrous iron, acid, manganese sulphate, and 4 cc. of indicator, again titrate. The difference between the two readings gives the reducing value of 2 cc. of the diphenylcarbazide. This scheme of titration of the blank allows a more rapid titration. Subtract the volume required for the blank from the original volume of dichromate and calculate the per cent of iron in the sample.

Series III. contains the results obtained with four iron ore samples from the Lake Superior region. The "per cent iron" column in each case contains the per cent of iron obtained by the permanganate method.

Several series of analyses, some with very small, others with larger amounts of iron, were made with results which check closely. With very small quantities of iron it is better to use a smaller quantity of indicator than with high iron content, adding some ferric chloride as in the blank determination. Titration of small amounts of iron should be made slowly with thorough agitation of the solution.

A solution of the indicator has a tendency to decompose slowly when exposed to the air because of oxidation, hence solutions should be kept in well-stoppered bottles. Under ordinary laboratory conditions a solution should be prepared fresh every few days unless protected from the action of the air. We have kept indicator solutions several months in an atmosphere of carbon dioxide without appreciable decomposition. However, the only apparent

SERIES III.—Iron Ores.

No.	Per cent iron.	Per cent found.	Deviation.
1.	64.84	64.77	0.07
2.	64.84	64.85	0.01
3.	64.84	64.75	0.09
4.	64.84	64.71	0.13
5.	64.84	64.74	0.10
6.	64.84	64.75	0.09
7.	64.84	64.76	0.08
8.	64.84	64.95	0.11
9.	64.84	64.70	0.14
10.	64.84	64.72	0.12
11.	64.84	64.79	0.05
1.	62.33	62.47	0.14
2.	62.33	62.39	0.06
3.	62.33	62.52	0.19
1.	66.29	66.48	0.19
2.	66.29	66.38	0.09
3.	66.29	66.65	0.36*
4.	66.29	66.29	0.00
5.	66.29	66.34	0.05
1.	28.15	28.19	0.04
2.	28.15	28.24	0.09
3.	28.15	28.20	0.05

* The cause for this particularly high result was not known at the time of titration.

SERIES IV.

HCl.	Manganese solution.	Indicator.	FeCl ₃ .	0.1N K ₂ Cr ₂ O ₇ .
Cc.	Cc.	Cc.	Cc.	Cc.
20	10	5	0.16	1.10
20	10	5	0.50	1.02
20	10	5	1.00	1.00
20	10	5	5.00	0.96
20	10	5	10.00	1.04

difference is a lowering of the reducing power and a corresponding less intense colouration during titration, hence a larger amount of the partially oxidised indicator is necessary to give the same effect as a fresh or protected solution. Series IV. contains the tabulated results of a number of blanks titrated with a constant amount of indicator which has been exposed to the air in a bottle with the stopper removed. This is a portion of the same indicator solution employed several days previous in Series I. and II.

Conclusions.

1. The end-point is an excellent one.
2. The indicator is a reducing agent and is oxidised by the dichromate during the process of titration. A blank determination must be made to ascertain this reducing power.
3. With the above modification the method is applicable to the analysis of ores for their iron content.
4. Small amounts of iron can be determined within the accuracy of the other methods in common practice.
5. In all likelihood the principle involved can be utilised in a number of other analyses. This point is being investigated.

The oxygen ratio existing between the oxidising agent and the indicator as obtained by different methods, the chemical reaction involved in causing the colour change titration, and the use of other compounds similar to diphenylcarbazide, especially those containing double bonds between the nitrogen atoms, are being likewise investigated.

We desire to express our appreciation to Dr. Benton Dales for his interest in the work throughout this investigation.—*Journal of the American Chemical Society*, xxxv., No. 2.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

THE WORLD'S PRODUCTION OF PETROLEUM IN 1913.

According to statistics that have been published for the first three quarters of the year 1913 concerning the exploitation of the different petroliferous regions of the whole world, it is seen that all the records established hitherto have been beaten. A comparative statistic of the last five years shows that the world's production has gone on steadily increasing. In 1912, the countries producing petroleum supplied 351,178,236 barrels of 42 gallons each, which makes 3,190,383 waggons of petroleum of 10,000 litres each. The increase which the petroliferous production of 1913 will show will certainly be due to the formidable gain registered by the output of California and of the naphtha fields of Kansas and Oklahoma. It is the United States that holds the first place among the countries producing petroleum. Their annual production exceeds 220 millions of barrels, and is 64 per cent of the whole world's production. Russia comes next, with 70 millions of barrels and a percentage of 19.37. These two countries alone represent, then, about 82 per cent of the petroliferous production of the whole world. The third place is held by Mexico, a country that has only just lately come to the front as a producer of petroleum. The part it contributes is 4.71 per cent. Roumania and the Dutch Indies are closely matched for the fourth and fifth places, with a rate of 3.70 per cent and 3.09 per cent in the naphthaiferous production of the world. Still another country on which geologists found great hopes for the future in what concerns petroleum is the Argentine Republic, the naphtha beds of which have up till the present time been very little explored.

A VOTING MACHINE.

The secret of votes is one of the most difficult things to obtain. The isolators that are to be brought into use at the next general legislative elections, and that were tried quite recently at Ivry sur Seine, near Paris, are very imperfect when they are compared with the automatic electoral machine devised by an engineer, M. Stefan Russo. The advantages of this new machine are numerous. It assures the secret of the vote even in the middle of a public square; it suppresses the voting ticket that permits cheating; it likewise suppresses the counting of the votes, often very long and the cause of numerous quarrels; it also permits the illiterate to vote; it obliges the elector to perform his duty as a citizen; it regulates the electoral operations automatically. Lastly, it is extraordinarily rapid, since 10,000 voters were able to vote in less than six hours, including the counting of the votes. The electoral cabin has one single door, over which is a register counting the number of electors who cross the threshold. Several lists are placed in the inside of the cabin, according to the number of political parties that are represented at the election. Every list mentions the party to which it is attributed; conservatives, liberals, radicals, socialists, and a special sign for each of them, destined for the illiterate. Above each slip, into which must be pressed a knob that has the form of a cylinder, are placed the photographs of the candidates and their names. To vote the elector must press on one of the knobs, which will only return to its primitive position when once the door of the cabin is open. So it is quite impossible to vote twice for the same candidate. Then, again, the door of the cabin can only be opened if the elector has completely fulfilled his electoral duty, which he cannot refrain from doing when once he has entered the cabin. If he has to vote for three deputies or five municipal councillors, the apparatus regulated for three or five obliges him to vote three or five times. At the same time, M. Russo's machine does not allow of voting for more candidates than is required. When the voting is ended, the president can immediately know the results of the polling. By means of a key he raises the plate bearing the photographs of the candidates. Under-

neath another slab appears bearing the same photographs with below each of them the number of votes obtained by the different candidates. The counting of the votes is thus ended. The electoral machine can be easily applied to all sorts of combinations. A regulating system enables the apparatus to be easily regulated to vote for a variable number of seats. It would even be quite easy to adapt the machine to vote for the proportional representation.

THE LIMIT OF FATIGUE.

Professional fatigue can be measured from the variations of the tracing or sketch of the movements of the heart. According to the experiments of M. Jules Amar explained by Prof. Dastre, it has been seen that as the power developed by the muscles increases the form of the cardiograms is changed. Their summit becomes more and more pointed. The undulation on the right that is supplied by the contraction of the heart lowers progressively. After the contraction that drives back the blood an aspiration is produced, the value of which goes on increasing. In all works of strength, carrying of burdens up staircases, fatiguing walking, running, work with the hammer, M. Amar has noticed curves that have an aspect identical to the physiological limit of fatigue.

THE FISH OF MADAGASCAR.

M. Edmond Perrier, Director of the Paris Natural History Museum, in the name of M. Pellegrin, Professor of the Museum, has presented a paper concerning the fresh water fish of Madagascar. M. Pellegrin has especially studied the *atherinides*, alimentary fish, of great economical importance for the large African Island. These fish came from the sea and have gradually become acclimatised in the fresh water of the rivers and lakes.

THE RETURN TO THE TYPE.

The question of naturalised foreigners is one that for some considerable time past has been preoccupying our sociologists. In a country like France, in which the birth rate is decreasing or at least stationary, it seemed to some that there would be a danger for the race in the penetration into the national territory of a large number of individuals natives of other countries. The danger, however, would not exist and would doubtless be transformed into a benefit if these foreigners intermarried with our compatriots. M. J. Lammonier, indeed, showed at the last meeting of the French Eugenic Society that the children from these mixed unions "resemble more the parent, whatever the sex may be, in whose original country they are born and live, rather than the other one." In other words, human half-breeds return with great rapidity to the ancestral type represented by the ascendants who lived in the country in which the half-bred or mongrel race was born. From this it results that foreigners married in France and living in this country have a posterity which becomes Frenchified without delay and definitely. Thus, by favouring the marriage and establishment of desirable, that is to say, healthy foreigners, according to the data of Dr. Lammonier, we might hope to palliate in a certain measure the threatening depopulation. Before the great difficulty of finding efficacious and applicable means for this end it would doubtless be well not to neglect this unexpected remedy.

Royal Institution.—On Tuesday next, March 3, at 3 o'clock, Sir John H. Biles begins a course of lectures on "Modern Ships"—(1) Smooth Water Sailing; (2) Ocean Travel; (3) The War Navy; and on Thursday, March 5, Prof. C. F. Jenkin delivers the first of three lectures on "Heat and Cold—Modern Applications, Theory of Caloric, Heat Engines, Freezing Machines, &c." The Friday Evening Discourse on March 13 will be delivered by Sir Walter R. Lawrence on "An Indian State"; and on March 20, by Lord Rayleigh on "Fluid Motions."

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 12, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Chemical Action that is Stimulated by Alternating Currents." By S. G. BROWN.

This paper describes experiments on the effects produced by passing a rapid alternating current through simple voltaic cells, the general effect being to stimulate chemical action and to cause the cells to give a greater supply of continuous current which otherwise could not be produced.

The alternating current will prevent a cell from polarising, or, if the exposure of the zinc anode is small, and the continuous current delivery restricted by this means, will increase the current by stimulating a greater chemical action between this pole and the electrolyte.

This latter action depends greatly upon the alternating current density, and if this is sufficiently high the chemical action induced may be sufficiently intense to oxidise any known metal forming the anode.

It is thought that this phenomenon is one of wide application and may explain the working of the Branley coherer.

"Effect of the Gangetic Alluvium on the Plumb-line in Northern India." By R. D. OLDHAM, F.R.S.

The depression occupied by the Gangetic alluvium along the southern face of the Himalayas, as determined by geological observation, has a nearly vertical face on the north, and a floor sloping upwards in a southerly direction to the surface. The depth at the northern margin is from 15,000 to 20,000 feet, and the width of the effective depression ranges up to about 200 miles: the density of the material filling this trough is not far from an average value of 2.1, that of the rocks forming the Himalayan range and the floor of the trough being about 2.7. The effect of the defect of mass in the Gangetic depression is calculated and shown to be capable of producing about 30" of northerly deflection of the plumb-line at the margin of the range, a deflexion which drops rapidly on either side of the margin but more rapidly to the south than the north. At 20 to 30 miles south, the distance depending on the width of the trough, it becomes zero, and at greater distances is replaced by a southerly deflexion.

It is shown that the deflexions so produced agree very closely with the residuals, or deflexions not accounted for by the visible topography, as calculated by Major H. L. Crosthwait for stations near or south of the Himalayan boundary. At stations to the north the data for comparison are not available.

"Note on the Origin of Black Body Radiation." By G. W. WALKER, F.R.S.

This is a supplement to my paper on the same subject, recently communicated to the society, in which I showed that an empirical radiation function—

$$k\theta^3 \left(\frac{\lambda\theta}{\lambda^2\theta^2 + n^2} \right)^4$$

gave an exceedingly good representation of the experimental data.

It is now shown that arbitrary disturbances, all of the type $te^{-n\theta}$, lead by Fourier resolution to precisely the above form of energy distribution.

This form of disturbance may be interpreted as a solution of the equation—

$$\ddot{x} + 2n_0\dot{x} + n_0^2x = 0$$

which represents the motion of a strictly aperiodic dynamical system.

"Transmission of Electric Waves along the Earth's Surface." By Prof. H. M. MACDONALD, F.R.S.

A series is obtained which represents the magnetic force at any point on the surface when the oscillator is also on the surface; the series converges rapidly for large values of θ , and for not very large values the first term is a sufficient approximation. For small values of θ the series converges very slowly. Tables showing the form in amplitude with increase of distances have been calculated for different wave-lengths.

"Transparence or Translucence of the Surface Film produced in Polishing Metals." By G. T. BEILBY, F.R.S.

Earlier observations on translucence in these films are confirmed by the further study of the film on polished copper. Minute pits caused by gas bubbles in the metal are shown to be covered by a translucent blue film through which rays of light reflected from the concave surface of the pit are seen as red spots. By the action of a solvent the film covering the pits can be completely removed, or it can, if desired, be so reduced in thickness that it becomes perfectly transparent. In either case the whole inner surface of the pit can be seen distinctly.

"A Thermomagnetic Study of the Eutectoid Transition Point of Carbon Steels." By S. W. J. SMITH, D.Sc., and J. GUILD.

The magnetic properties of steel at temperatures near the eutectoid transition point (A_1) seemed to deserve further examination. Simultaneous observations of intensity of magnetisation and of temperature were made over various ranges of heating and of cooling in different magnetic fields. Nine steels containing percentages of carbon ranging between 0.1 and 1.5 were used. Each steel contained about 0.2 per cent, or less, of silicon and of manganese.

It was found that the temperature corresponding with the beginning of the transformation of the eutectoid during heating (A_{11}) could be fixed within $\pm 1^\circ$ C. under suitable conditions. This temperature was 735° C. as read by our thermometers, which however were better adapted for comparative measurements than for determination of absolute values. It was the same for all the steels.

The reasons why this temperature, although constant, must be higher than the true equilibrium temperature are discussed. The existence of the lag and of its causes is also shown by direct experiment. A thermomagnetic method of estimating the true equilibrium temperature is described and used.

The inverse change from solid solution to eutectoid during cooling (A_{11}) is also clearly shown upon all the thermomagnetic curves. The conditions under which the eutectoid separates are, however, seen to be more complex than those under which it disappears. The temperature of the change is no longer constant. It is highest in the hypo-eutectoid steels, and it diminishes continuously in the hypo-eutectoid steels with the percentage of carbon. The range is from about 725° to about 695° C.

The cause of this phenomenon is discussed.

"Note on Osmotic Pressure." By W. R. BOUSFIELD, M.A.

The osmotic pressure of a solution is the pressure under which the internal vapour pressure of the solution is raised to equality with the vapour pressure of the pure solvent. It is the compression of the solution which raises its internal vapour pressure. It is shown that the assumption that the molecular interspaces of a solution are filled with vapour, which there behaves as a perfect gas, leads to the same general relation between vapour pressure and osmotic pressure as is given by thermodynamical considerations. The anomalous fact that the osmotic pressure of a decinormal sucrose solution is found to be greater at 0° C. than at 5° C. is explained by reference to the constitution of water and the effect of compression upon the ice molecules.

CHEMICAL SOCIETY.

Ordinary Meeting, February 5, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

THE PRESIDENT referred to the loss sustained by the Society, through death, of Mr. Frank Baker and Mr. Frederick George Richards.

Certificates were read for the first time in favour of Messrs. Abdel Hameed Ahmad, B.Sc., The University, Edgbaston, Birmingham; Charles Wesley Bayley, 63, Caxton Road, Wood Green, N.; Robert Barclay Craig, 50, North Albion Street, Glasgow; Jaroslav Heyrovsky, B.Sc., 24, Agincourt Road, N.W.; Lawson John Hudleston, B.Sc., 68, Parliament Hill, Hampstead, N.W.; Arthur Ulysses Newton, B.Sc., 37, Nertherhall Gardens, Hampstead, N.W.; Lal Behary Seal, Third Assistant Chemical Examiner, Rangoon, Burma; Norman Cecil White, B.A., B.Sc., 35, Spencer Park, Wandsworth, S.W.

Of the following papers, those marked * were read:—

*25. "Existence of Racemic Compounds in the Liquid State." By CLARENCE SMITH.

The investigation, by the Ramsay-Shields' method, of the existence of racemic compounds in the liquid state (Mitchell and Smith, *Trans.*, 1913, ciii., 489) has been extended to include substances which contain a hydroxyl group. Not infrequently such substances are associated in the liquid state. The dissociation produced by rise of temperature is manifested by an abnormally large rate of decrease of the molecular surface energy, so that the value of k increases with rise of temperature, and does not remain constant (or decrease slightly), as is the case with unassociated liquids. If, therefore, the optically active modifications of a liquid are associated and the inactive form is an equal molecular mixture of the active forms, the expectation is legitimate that the k values of all the modifications will increase at the same rate with rise of temperature, whereas if the inactive form is a racemic compound (associated or not), material differences will be observed in the k values of the inactive and the active liquids. Unfortunately, all the liquids, the active forms of which are at present at the author's command, have proved to be unassociated between 0° and 90°, so that the preceding method of proof is unavailable. However, the practically constant and not materially different k values of the active and the inactive modifications of each of the substances examined prove, as in the case of the pinenes and the limonenes (*loc. cit.*), that the inactive modifications are not liquid racemates.

The following values of k (mean of four values between 10° and 80°) have been calculated:—Methyl- β -phenylethylcarbinol, dl -form 2.185, d -form 2.015, l -form 2.15; methylhexylcarbinol, dl -form 2.045, d -form 1.975, l -form 1.91; phenylethylcarbinol, dl -form 2.02, l -form 1.96; methyl β -hydroxy- β -phenylpropionate, dl -form 2.33, d -form 2.395.

DISCUSSION.

Dr. DUNSTAN pointed out that Mr. Thole had already shown that the inactive carbinols prepared by Dr. Pickard were dl -mixtures and not racemic compounds. He further stated that, even when racemic compounds had been found to exist in solution, the quantity present in equilibrium with the active components was always very small.

*26. "The Water Gas Equilibrium in Hydrocarbon Flames." By GEORGE WILLIAM ANDREW.

The author has examined the equilibrium conditions as regards the reversible system $\text{CO} + \text{OH}_2 \rightleftharpoons \text{CO}_2 + \text{H}_2$ in hydrocarbon flames by exploding at varying initial pressures homogeneous mixtures of such hydrocarbons as methane, ethane, and ethylene with quantities of oxygen insufficient for complete combustion, but sufficient to prevent any deposition of carbon on explosion (for example,

$\text{CH}_4 + \text{O}_2$, $2\text{CH}_4 + 3\text{O}_2$, $2\text{C}_2\text{H}_6 + 3\text{O}_2$, $2\text{C}_2\text{H}_6 + 5\text{O}_2$, $\text{C}_2\text{H}_4 + 2\text{O}_2$, &c.).

The results prove that, notwithstanding the very different maximum flame temperatures in the various experiments, the equilibrium ratios $\frac{\text{CO} \times \text{OH}_2}{\text{CO}_2 \times \text{H}_2}$ in the cooled

products were nearly constant throughout the series, and practically identical with the value found by H. B. Dixon in his well known experiments on the division of oxygen between CO and H_2 in flames, thus:—

Mixture.	Mean "K" = $\frac{\text{CO} \times \text{OH}_2}{\text{CO}_2 \times \text{H}_2}$
$\text{CH}_4 + \text{O}_2$	3.98
$2\text{CH}_4 + 3\text{O}_2$	3.98
$2\text{C}_2\text{H}_6 + 3\text{O}_2$	4.12
$2\text{C}_2\text{H}_6 + 5\text{O}_2$	3.63
$2\text{C}_2\text{H}_4 + 3\text{O}_2$	3.43
Mean	3.83

It would thus appear that the experimentally determined equilibrium constant "K" does not correspond with the maximum flame temperature, but with some lower temperature in the "cooling curve" when the gases cease to react rapidly. This temperature is identified as lying somewhere between 1500° and 1600°. It was further shown that so rapidly does the equilibrium in the system $\text{CO} + \text{OH}_2 \rightleftharpoons \text{CO}_2 + \text{H}_2$ adjust itself to the falling temperature, during the cooling period down to the said temperature, that even the deposition of carbon or the recurrence of considerable quantities of methane in the products has little or no influence on the said equilibrium.

27. "The Absorption Spectra of the Vapours and Solutions of Various Substances containing Two Benzene Nuclei." By JOHN EDWARD PURVIS.

The observations prove that all the various vapour bands of benzene are obliterated in such compounds as diphenyl, diphenylmethane, diphenylamine, diphenyl ether, &c., and all the various vapour bands of aniline in such compounds as azobenzene, azoxybenzene, benzidine, &c. In every instance the vapour bands and the solution bands are similar.

28. "The Oxidation of some Benzyl Compounds of Sulphur. Part II. Benzyl Tetrasulphoxide." By JOHN ARMSTRONG SMYTHE.

When benzyl tetrasulphide is oxidised with hydrogen peroxide, benzyl tetrasulphoxide is formed in quantitative yield. Benzyl trisulphide, on oxidation, gives the same compound, in addition to benzaldehyde, sulphuric acid, and benzyldisulphonic acid.

Benzyl tetrasulphoxide is a somewhat unstable compound, melting at 134–139°, and decomposing at its melting-point into benzyl disulphide and sulphur dioxide. When heated in solution, or treated with a variety of reagents, it decomposes into benzyl disulphoxide, sulphur, and sulphur dioxide, and the subsequent reaction of these products gives the clue to a number of changes which the compound undergoes.

Excess of hydrogen peroxide oxidises the tetrasulphoxide to sulphuric and benzyldisulphonic acids; some benzaldehyde is also formed, as is the case with all the polysulphidic compounds of benzyl on oxidation.

Other reactions, which serve to bring out the relationship of the tetrasulphoxide with other sulphur compounds, were described.

29. "The Reaction between Iodine and Aliphatic Aldehydes." By HARRY MEDFORTH DAWSON and JOSEPH MARSHALL.

According to Chautard (*Ann. Chim. Phys.*, 1889, [6], xvi., 145), iodine reacts with the aliphatic aldehydes in alcoholic solution in the presence of iodic acid, and moniodo-substitution products are formed. In some cases the substances obtained are supposed to be α -derivatives, whilst in others it is claimed that β -substitution products are produced. In view of the fact that evidence has been

obtained that halogen substitution in the aldehydes is preceded by isomeric change, and that β -substitution products cannot be accounted for, if this is the mechanism of the reaction, it was considered advisable to repeat some of Chautard's experiments.

The authors find that there is no evidence of the formation of β -iodopropaldehyde, the properties of the substance obtained being in entire agreement with the supposition that it is the α -iodo-derivative.

The statement that alkyl esters are formed when the iodoaldehydes are acted on by silver acetate is also not confirmed by the author's observations. In the case of iodoacetaldehyde, no trace of ethyl acetate was found, and the product appears to be acetylglycollaldehyde.

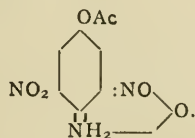
30. "The Erosion of Lead." By JOHN FRANCIS LIVERSEECE and ARTHUR WILLIAM KNAPP.

The authors have examined the action of a slightly alkaline natural water on strips of sheet lead under the conditions of the test proposed by Houston (area of 6.45 sq. cm. of lead exposed to 10 cc. of water in a test-tube), save that a duration of one day was preferred to the seven or fourteen days suggested by Houston. It was found that erosion was due to the action of oxygen in the presence of water. Carbon dioxide in an amount up to 1 per cent by volume produced little effect on the amount of erosion; when 2 or more per cent of carbon dioxide was present, erosion no longer occurred, for the liquid remained clear, and lead was dissolved (in amount less than that removed by erosion). The amount and kind of erosion was chiefly dependent on the alkalinity of the water. With alkalinity expressed as parts of calcium carbonate per 100,000 of water, (a) lime giving 3 to 9 parts of alkalinity reduced the erosion, but larger and smaller quantities slightly increased it; (b) calcium carbonate giving 4 parts of alkalinity greatly reduced erosion; (c) calcium carbonate giving only 2 parts of alkalinity practically prevented it. Variations in the amount of organic matter did not influence the erosion. Exposure to glass lowered the erosive quality of the water, but filtration through sand did not.

The amount of lead eroded was less the greater the distance from the lead to the water surface, and was generally proportional to the area of the surface of the lead exposed, and independent of the volume of the water.

31. "Acylation as Influenced by Steric Hindrance: the Action of Acid Anhydrides on 3:5-Dinitro *p*-aminophenol." By RAPHAEL MELDOLA and WILLIAM FRANCIS HOLLELY.

The known *N*-acetyl derivative of the above dinitro-aminophenol is best prepared by starting from the diacetyl derivative and hydrolysing the latter by cold dilute sodium hydroxide solution. The authors find that this dinitro-*p*-aminophenol has the remarkable property of becoming acylated at the hydroxyl group with extreme facility, the *O*-acetyl derivative being formed by simply boiling the dinitro-compound with a little acetic anhydride diluted with acetic acid for half-an-hour or less. In these circumstances the amino-group is unattacked, and the isomeric *N*-acetyl and *O*-acetyl derivatives can accordingly be prepared by regulating the conditions. The authors attribute this property to the extreme protection of the amino-group by the ortho-nitro-groups, aided probably by an ortho-quinonoid structure due to the existence of an "inner salt" structure:—



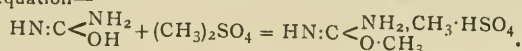
Reasons were given, based chiefly on the marked difference in colour between the isomerides and the character of their absorption spectra (photographed by Dr. J. T. Hewitt), for assigning the above formula to the *O*-acetyl derivative. The authors conclude that all the nitro-

derivatives of the aminophenols in which there is a nitro-group adjacent to an amino-group are best represented as "inner salts" of the above type.

32. "The Constitution of Carbamide. Part I. The Preparation of isoCarbamides by the Action of Methyl Sulphate on Carbamides." By EMIL ALPHONSE WERNER.

It was pointed out that hitherto carbamide has not been known to yield by any direct reaction derivatives of the type HN:C(OR)NH_2 , in contrast to thiocarbamide, which readily affords the sulphur analogues HN:C(SR)NH_2 by the direct reaction with the alkyl haloids. So far, isocarbamides of the types HN:C(OR)NH_2 , RN:C(OR)NH_2 , and RN:C(OR)NHR have been obtained by the union of cyanamides and alcohols in the presence of hydrogen chloride or sodium ethoxide (Stieglitz and McKee (*Ber.*, 1900, xxxiii., 1518; and Bruce, *Fourm. Am. Chem. Soc.*, 1904, xxvi., 419, 449).

It was shown that methylisocarbamide and its substituted derivatives may be readily prepared from carbamide and substituted carbamides by the aid of methyl sulphate; the change takes place quantitatively in accordance with the equation—



Whilst in the case of carbamide the reaction is liable to become very violent unless the temperature is carefully controlled, the change proceeds quite smoothly with the substituted derivatives. The free bases may be isolated by treating the product with sodium hydroxide solution and extracting with ether or alcohol.

The decomposition of methylisocarbamide methyl hydrogen sulphate, and the substituted derivatives has been examined, and the results have furnished interesting confirmatory evidence in support of the author's views regarding the constitution of carbamide and substituted carbamides; thus, whilst the methylisocarbamide salt and the derivatives of the types $\text{HN:C} \begin{smallmatrix} \text{NR}_2 \\ \text{O-CH}_3 \end{smallmatrix}$ and

$\text{HN:C} \begin{smallmatrix} \text{N:R''} \\ \text{O-CH}_3 \end{smallmatrix}$ afforded cyanuric acid and mono-*N*-methylcyanuric acid as part of the decomposition products, neither of these acids was obtained from the derivatives of the type $\text{RN:C} \begin{smallmatrix} \text{NH}_2 \\ \text{O-CH}_3 \end{smallmatrix}$ prepared from the mono-substituted carbamides.

The interaction of carbamide and methyl sulphate carried on slowly to the stage of the decomposition of the isocarbamide salt may be used as a quick and simple method for the preparation of pure methylamine. If the reaction is allowed to become very violent some dimethylamine is formed.

33. "A New Formula for the Latent Heat of Vapours." By MALCOLM PERCIVAL APPLEBEY and DAVID LEONARD CHAPMAN.

A new formula for the heat of vaporisation of liquids, of which a preliminary account has already been published (*Proc.*, 1913, xxix., 24) was deduced from the thermodynamic principles and van der Waals' equation. The latent heats of the vapour of some common non-associated and associated compounds were calculated with the aid of the formula, and the values obtained were compared with those experimentally determined by S. Young (*Sci. Proc. Roy. Dubl. Soc.*, 1910, xii., 414).

34. "The Electro-deposition of Zinc at High Current Densities." By JOHN NORMAN PRING and URLYN CLIFTON TANTON.

At certain very high current densities the electro-deposition of zinc can be effected in presence of a high concentration of free acid. Under these conditions the ratio of zinc to hydrogen liberated actually increases with the acid concentration up to a certain value, and also increases with the current density. In this way, with a concentration of sulphuric acid of about 15 grms. per 100 cc. and a

current density of between 20 and 50 ampères per sq. dcm. the metal can be deposited with an efficiency of about 95 per cent.

With lead anodes this electrolysis is achieved with a potential difference about 5 volts and with zinc anodes 3 volts.

The presence of small quantities of colloidal matter exerts a marked effect on this reaction, and enables the production of bright adherent deposits. The presence of the colloid also enables the application of a higher current density, and in this way raises the current efficiency.

In these solutions a very strong retardation was observed in the deposition of iron present in the electrolyte. On account of this, considerable quantities of this metal in the electrolyte caused very little contamination of the zinc.

The results obtained could not be entirely ascribed to effects of over-voltage, or surface tension, or viscosity of the electrolyte, and are probably mainly determined by influences which control the rate of the reactions involved in the change from the ionised to the free element.

The results obtained in this work indicate the most favourable conditions under which zinc can be obtained from commercial solutions, either with a view to the recovery of the metal or to its application for the purpose of electroplating.

35. "The Ageing of Alloys of Silver and Tin." By WILLIAM ARTHUR KNIGHT.

The author has investigated the ageing of filings of alloys of silver and tin, and the densities of unaged and aged filings of the alloy Ag_3Sn . The ageing of filings of the alloy Ag_3Sn is not accompanied by a detectable change of weight, and this applies whether the ageing is carried out in coal-gas or in air. Ozone and hydrogen peroxide did not oxidise these filings at room temperature, and, further, after treatment with these oxidising agents, the filings were still unaged. From these experiments, in conjunction with others previously published, the hypothesis that the ageing of these filings is due to superficial oxidation was shown to be untenable. It was found that hydrogen sulphide at room temperature had no effect on the state of ageing of the filings. The phenomenon of ageing becomes less pronounced when the content of silver in the alloy exceeds 75 atoms per cent, solid solutions of silver in the compound Ag_3Sn thus having the same effect as the free tin in those alloys which contain less than 75 atoms per cent of silver. Density determinations showed that the density of aged filings of the alloy Ag_3Sn is greater than that of unaged filings; thus, as there is no increase in weight, there must be a contraction in volume on ageing. Dilatometer measurements confirmed this contraction, although the results did not agree accurately with those deduced from density determinations.

36. "The Action of Phosphorus Pentachloride on the Esters of Glycric Acid: Optically Active $\alpha\beta$ -Dichloropropionates." By PERCY FARADAY FRANKLAND and ANDREW TURNBULL.

From *lævorotatory* methyl, ethyl, *isobutyl*, and *heptyl* glycerate respectively the authors have obtained the corresponding $\alpha\beta$ -dichloropropionates, of which the methyl compound was *dextro*- and the others *lævorotatory*. The *dextrorotation* of methyl $\alpha\beta$ -dichloropropionate increases with rise of temperature, whilst the *lævorotation* of the others diminishes in the same circumstances. There would appear, therefore, to be no doubt that all of these dichloropropionates have the same configuration.

A more highly chlorinated inactive compound was in each case also obtained, having the molecular formula $\text{C}_3\text{H}_2\text{Cl}_5\text{OR}$, of which the probable constitution is $\text{CH}_2\text{Cl}-\text{CCl}_2-\text{CCl}_2\text{OR}$ or $\text{CHCl}_2-\text{CHCl}-\text{CCl}_2\text{OR}$, in which R stands for methyl, ethyl, *isobutyl*, and *heptyl* respectively (see also *Trans.*, 1913, ciii., 718).

(To be continued).

PHYSICAL SOCIETY.

Annual General Meeting, February 13, 1914.

Prof. C. H. LEES, F.R.S., Vice-President, in the Chair.

THE Report of the Council was taken as read.

Mr. T. SMITH asked leave to draw attention to certain disadvantages of the present method of electing the Council. For reasons which he gave he thought there ought to be a change in the method of ballot. He suggested that the Council should issue its list earlier than at present, and allow Fellows to send in other nominations if they so desired. The final balloting list should contain the names of everyone nominated. He thought that this would lessen the risk of inadequate representation of any important branch of physics upon the Council and of more than adequate representation of others. He saw no reason why the statutes should not be altered if necessary to make this possible.

The CHAIRMAN said he had no doubt that the Council would carefully consider Mr. Smith's suggestions.

Mr. E. F. ETCHHELLS thought it would be advisable on the present occasion, before the committee on scientific nomenclature had got to work, to emphasise the importance of adopting the system already accepted by engineers. He outlined some of the principles, and hoped that the committee would make itself familiar with the existing schemes before reaching any decision.

Dr. ECCLES assured the speaker that this was being done.

The Treasurer's Report was then read by Mr. DUDELL.

The reports of the Council and Treasurer were adopted.

Votes of thanks to the Auditors, the Officers and Council, and the Governing Body of the Imperial College were carried unanimously, the respective proposers and seconders being Dr. G. W. C. KAYE and Mr. E. F. ETCHHELLS, Mr. C. W. S. CRAWLEY and Mr. A. CAMPBELL, and Prof. J. W. NICHOLSON and Major O'MEARA.

The following is the list of officers elected for the ensuing year:—

President—Sir J. J. Thomson, O.M., D.Sc., F.R.S.

Vice-Presidents (who have filled the office of President)

—Prof. G. C. Foster, F.R.S., Prof. W. G. Adams, M.A., F.R.S., Prof. R. B. Clifton, M.A., F.R.S., Prof. A. W. Reinold, C.B., M.A., F.R.S., Prof. Sir Arthur W. Rücker, M.A., D.Sc., F.R.S., Sir W. de W. Abrey, R.E., K.C.B., D.C.L., F.R.S., Prin. Sir Oliver J. Lodge, D.Sc., F.R.S., Prof. S. P. Thompson, D.Sc., F.R.S., R. T. Glazebrook, D.Sc., F.R.S., Prof. J. H. Poynting, M.A., F.R.S., Prof. J. Perry, D.Sc., F.R.S., C. Chree, Sc.D., F.R.S., Prof. H. L. Callendar, M.A., F.R.S., Prof. A. Schuster, Ph.D., F.R.S.

Vice Presidents—Prof. T. Mather, F.R.S., A. Russell, M.A., D.Sc., F. E. Smith, R. S. Whipple.

Secretaries—W. R. Cooper, M.A., 82, Victoria Street, S.W., S. W. J. Smith, M.A., D.Sc., Imperial College of Science and Technology, S. Kensington.

Foreign Secretary—R. T. Glazebrook, D.Sc., F.R.S.

Treasurer—W. Duddell, F.R.S., 56, Victoria Street, S.W.

Librarian—S. W. J. Smith, M.A., D.Sc., Imperial College of Science and Technology.

Other Members of Council—W. H. Eccles, D.Sc., Sir R. A. Hadfield, F.R.S., Prof. G. W. O. Howe, M.Sc., Prof. J. W. Nicholson, M.A., D.Sc., Major W. A. J. O'Meara, C.M.G., C. C. Paterson, Prof. O. W. Richardson, M.A., D.Sc., F.R.S., Prof. the Hon. R. J. Strutt, F.R.S., W. E. Sumpner, D.Sc., R. S. Willows, M.A., D.Sc.

Assist. Secretary and Reporter—J. Guild, A.R.C.S., D.I.C.

A Paper entitled "*On the Moving Coil Ballistic Galvanometer.*" By R. LL. JONES, M.A., was read by Mr. A. CAMPBELL.

The author first considers the mathematical theory of a moving coil galvanometer in which the damping is such as to make the motion non-oscillatory; then an account is given of some observations on a galvanometer which confirm some of the deductions from the theory, and the results obtained are applied to find the relation between the galvanometer throw and the change of flux in the search coil which produces it.

DISCUSSION.

Prof. C. H. LEES thought it likely that with a highly damped galvanometer the creeping at the end would create a difficulty as to what reading to take.

Prof. T. MATHER stated that the creep presented no difficulty, since it was easy to get the maximum deflection reached. The real difficulty was in getting the true zero.

Mr. A. CAMPBELL mentioned that although the case of the strongly damped galvanometer when used with a search coil did not appear to be treated in any English text-book, he had found it described in Kohlrausch's "*Lehrbuch der praktischen Physik*" (10th edition, 1905).

A Paper "*On Vibration Galvanometers of Low Effective Resistance*" was read by Mr. A. CAMPBELL.

The mathematical theory of the motion of the moving coil of a vibration galvanometer is first given (partly following Wenner), and simple relations are shown to hold between the two resonance frequencies, the free frequency and the amplitude time constant. It is also shown how all the constants of the equation of motion can be deduced from observations of the direct and alternating-current sensitivities, the alternating voltage sensitivity, and the "dead" resistance. A complete table of the observed and deduced constants is given for a series of very small coils, the number of turns in these varying from 1 to 40. The current sensitivities range from 6 mm. to 160 mm. at 1 m. per microampere at 100 vibrations per second, the corresponding effective resistances being about 9 and 1500 ohms respectively. It is pointed out that the selectiveness (for given current) due to resonance is mainly determined by the absolute value of the "amplitude time constant"; the more sluggish a galvanometer is in settling to zero the more selective will it be.

DISCUSSION.

Dr. RUSSELL thought everyone was indebted to Mr. Campbell for popularising the resonance galvanometer. In the present Paper the use of the amplitude time constant struck him as being very neat.

Prof. G. W. O. HOWE pointed out that one method of determining the no-load losses of a motor was to cut off the supply and observe the rate of slowing down. From this the losses could be calculated and the efficiency found. This, in effect, was what Mr. Campbell did with the vibration galvanometer, and there seemed to be many analogous points in the two processes.

Mr. CAMPBELL thought Prof. Howe's analogy was extremely good. He added that a coil tested at 50 vibrations per second gave a current sensitivity of 500 mm. at 1 metre per microampere with an effective resistance of 2500 ohms.

A Paper "*On Vacuum-tight Lead Seals for Leading-in Wires in Vitreous Silica and other Glasses,*" was read by Dr. H. J. S. SAND.

The author has found out that lead which has been allowed to solidify in contact with glass will, if free from oxide, form a vacuum-tight joint with the latter. Owing to the very great firmness with which the metal adheres, and owing to its great plasticity, these joints can stand temperature changes without damage. When applied to quartz, the joints are usually made inside a tube in conjunction with a molybdenum wire seal as follows:—The tube is shaped so that the molybdenum wire can be placed loosely inside it. A short piece of the latter is later sealed into the quartz, whereas one of its ends pro-

jects a few millimetres into the space in which the lead seal is to be made. Connected with this space by a short capillary there is an upper chamber in which the piece of lead is placed. The air is first blown out with hydrogen, and the tube then closed at the top and evacuated to a pressure of a millimetre or two. The quartz is then softened and pinched on to the molybdenum wire. After this the lead is melted and allowed to filter from oxide through the capillary and run into the space shaped to receive it, which has been highly heated. Before it has solidified, the tube is broken at the top to allow the pressure of the atmosphere to force the lead well against the surface of the glass. The tube is then cut at a suitable place and a tinned leading-in wire introduced into the lead. Such seals have been successfully fitted to vacuum tubes, mercury lamps, &c., and when made as described have so far not been known to fail.

DISCUSSION.

Prof. C. H. LEES asked how the cost of the process compared with that of the ordinary platinum seals in the case of glass.

Dr. SANDS, in reply, stated that platinum seals could be made with such small quantities of platinum that it was hopeless to try to compete with them in point of cheapness.

NOTICES OF BOOKS.

The Sampling and Assay of the Precious Metals. By ERNEST A. SMITH, Assoc.R.S.M. London: Charles Griffin and Co., Ltd. 1913.

THIS treatise on the sampling and assay of the precious metals is intended for the use of both practical assayers and students, the requirements of the latter class of readers having been specially considered. It will be found admirable for both purposes, being thoroughly practical and comprehensive, and the descriptions of methods of sampling, and of the principles of the valuation and sale of ore and bullion, will be particularly valuable to assayers. "The precious metals" include gold, silver, platinum, and the platinum metals, and methods of determining them are described in considerable detail. The first eleven chapters deal with the general principles of assaying, the design and equipment of offices, the choice and use of apparatus, and the sampling of specimens, which latter subject is considered in much greater detail than is usual in books on metallurgy and assaying. The later chapters are devoted to the assay of gold and silver bullion, base bullion, alloys, and ores, and an adequate account is also given of the laboratory work of a cyanide mill.

A Practical Manual of Autogenous Welding (Oxyacetylene).

By R. GRANJON and P. ROSEMBERG. Translated by D. RICHARDSON, Wh.Ex., A.M.I.M.E. London: Charles Griffin and Co., Ltd. 1913.

THE process of autogenous welding by the oxyacetylene blowpipe was discovered not much more than twelve years ago, but it is already employed in thousands of workshops, and engineers and manufacturers have quickly realised its great value. The knowledge, however, of the principles involved is distinctly behind that of the practice, in this country at any rate, and hitherto no book in the English language has been obtainable which dealt with the theory and technology of the process. Hence there is no doubt but that this book will be warmly received. The original French work reached its second edition within a year of publication, and the translation has been made from the revised edition, which embodies all the latest advances. It is written mainly for the practical man, and full information is given relating to the materials, methods, and manipulation. Prices, weights, &c., are given in English as well as in French units, and the translator has added some notes relating to English regulations and practice.

Handbook on Petroleum. By Captain J. H. THOMSON and Sir BOVERTON REDWOOD. Third Edition. Revised and Added to by Major A. COOPER KEY and Sir BOVERTON REDWOOD, Bart. London: Charles Griffin and Co., Ltd. 1913.

IN the new edition of this widely used handbook for inspectors under the Petroleum Acts the chapter on sources of supply has been partly re written, and the accounts of the storage and distribution of petroleum products has been extended. It has not been found necessary to make many alterations in the chapters dealing with legislation, but the appendices have been brought down to date by the inclusion of the most recent orders.

Elementary Practical Chemistry. Part I. *General Chemistry.* By FRANK CLOWES, D.Sc. (Lond.), and J. BERNARD COLEMAN, A.R.C.Sc. Sixth Edition. London: J. and A. Churchill. 1914.

IN the sixth edition of this valuable book a new section has been added on phosphorus and some of its simpler compounds, silica, and the silicates and glass. It also contains two new sections on some of the common metals, in which the properties of and tests for the metals are given, and experiments involving the preparation and reactions of their salts are described. The text has also been revised throughout, but only very few and unimportant corrections have been found necessary.

The International Whitaker. London: J. Whitaker and Sons, Ltd. New York: The International News Co. 1914.

THIS handbook contains accounts of the government, finance, products, industries, commerce, &c., of all the countries of the world. It is issued at a very moderate price, and will be found invaluable for schools and colleges as a reference book, to correct or supplement the data given in geographical text-books. The information contained in it has been revised in every instance from official sources, and in many cases by Government Departments.

Carnotite, the Principal Source of Radium. By THOMAS F. V. CURRAN. 1913.

THIS pamphlet has been issued by Messrs. Curran and Hudson, dealers in radium products, radio-active ores, &c., and contains short accounts of the chemical nature and occurrence of carnotite. The cost of mining the ore is discussed, and its metallurgy and the extraction of radium are also described. The pamphlet contains in addition a brief account of the uses of radium, and abstracts of the report of the British Radium Institute, issued in 1913, and of the government publications of Austria-Hungary as to its employment in therapeutics.

The Manuring of Market Garden Crops. By BERNARD DYER, D.Sc., F.I.C., and F. W. E. SHIRVELL, F.L.S. New Edition. London: Vinton and Co., Ltd. 1913.

THIS book contains a detailed account of the authors' experimental work in market gardening at Hadlow, Tonbridge, which was begun in 1894. The main object of the work was to discover how far the large quantities of stable manure purchased by market gardeners are necessary, and in what circumstances artificial fertilisers can be substituted for them. A large variety of vegetable and fruit crops was investigated; in fact, practically all those commonly grown in England, and the results in the case of each individual crop are tabulated, illustrated, and discussed. Very precise practical recommendations are given, based upon the authors' experiments, and questions of cost are carefully considered. The book should be in the hands of all market gardeners, and the authors' advice on the use of artificial fertilisers will be of the greatest value, especially in view of the fact that it seems probable that stable manure will be an almost unobtainable article of commerce in the near future.

Ozonair Apparatus for Therapeutical Applications.

THIS pamphlet, issued by the Ozonair Company, Ltd., gives short non-technical descriptions of the forms of portable apparatus made for the production of ozone for inhaling, and disinfecting and deodorising purposes. Some details are included regarding the initial and running costs, the latter being described as almost negligible, and other pamphlets relating to other applications of the apparatus can be obtained from the offices of the company, 96, Victoria Street, Westminster.

Aichiken Commercial Museum, Nagoya, Japan.

THIS pamphlet contains some account of the aims and equipment of the Aichiken Commercial Museum, which the authorities of the city of Nagoya are strenuously trying to bring to the highest pitch of efficiency and usefulness. Nagoya has been called the Birmingham of Japan, and the museum is destined to be one of the largest and best equipped in the country. The account is written in what may be described as "credible" English, to borrow an expression from the text, and the illustrations are excellent. To celebrate the third anniversary of the opening of the museum an exhibition of samples, circulars, and catalogues is to be held from March 1 to April 30 of the current year. Foreign manufacturers are invited to forward exhibits, and further particulars may be obtained from the Museum.

CORRESPONDENCE.

SOME ANOMALOUS VARNISH VISCOSITIES.

To the Editor of the Chemical News.

SIR,—I shall be glad if some of your readers can explain the cause of some anomalous results obtained by me in the determination of viscosity of oil varnishes by means of a Doolittle's torsion viscometer. The varnish referred to here was a very thick black stoving varnish, and it was sought to determine the effect of increase of temperature upon its viscosity. The viscometer used is an application of the torsion pendulum, and is described in the *Journal. Am. Chem. Soc.*, 1883, clxxiii., 454, and in Allen's "Commercial Organic Analysis," vol. ii., part 2, p. 125. The "bob," which is immersed in the liquid, is a brass cylinder $2'' \times 1\frac{1}{4}''$, which is attached to a heavier brass weight with disc graduated in degrees (above it and out of the liquid), and the whole is suspended by a tempered steel wire of 0.295 mm. diameter (0.0116 inch) and 21 inches long.

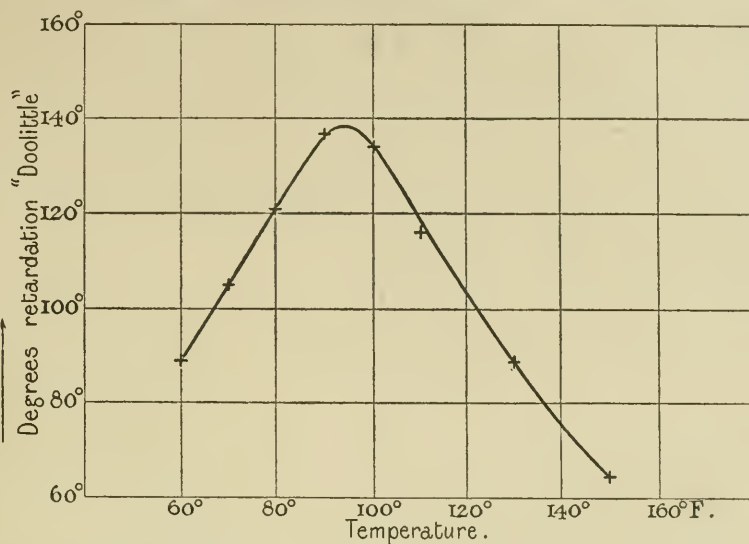
The "bob" being immersed in the liquid, the wire is rotated 360° and the cylinder allowed to swing free. The instrument measures the amount of damping between the first and second swings in the same direction, and this damping is read in angular degrees. Two tests are made in opposite directions to minimise any error which might be due to the instrument not having been adjusted to zero.

The effect of increase of temperature on a varnish is to cause it to become thinner, but it is here where the anomaly comes in. I give the figures obtained:—

Temperature (°F.)	60	70	80	90	100	110	130	150
Degrees retardation ..	..	..	89	105	121	137	134	116
							89	65

These results have been plotted in the accompanying graph.

It will be seen that an increase of temperature from 60° to 90° F. has increased the apparent viscosity, but from 100° to 150° F. the viscosity decreases in a normal manner. These results are not due to errors of experiment, because similar results have been obtained from other oil varnishes. Even gradual additions of oil of turpentine to a thick



Influence of Temperature upon Viscosity of a Black Stoving Varnish.

varnish has given similar increase to a maximum, and then a decrease. The viscosities, as a matter of fact, *do not* increase with rise of temperature, but the curious results here given are due to some physical property, which I should be glad to have explained.—I am, &c.,

THOMAS A. DAVIDSON.

"Ardlui," 37, Strathyre Avenue, Norbury, S.W.,
February 2, 1914.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

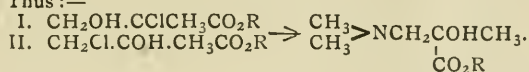
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de France.
Vol. xv.-xvi., No. 1, 1914.

Thermic and Cryoscopic Studies of Mixtures of Benzene and Ethyl Alcohol.—F. Viala.—The specific heat of a mixture of ethyl alcohol and benzene is appreciably greater than the value obtained by calculation; there is a relation between the specific heat of the mixture and its heat, and the former seems to be a function of the concentration. The molecular association of ethyl alcohol in solution in benzene increases with the concentration. In dilute solution all the molecules are simple. The molecular weight is given by $C_2H_6O = 46$. In concentrated solution all the molecules are double, and the molecular weight is 92.

Double and Complex Cyanates.—Paul Pascal.—The author has demonstrated the existence of four cyanates derived from uranium:—1. The greenish yellow complex salt, $[\text{UO}_2(\text{CNO})_4]\text{K}_2$. 2. Its normal product of hydrolysis, $(\text{UO}_2)_2(\text{CNO})_5\text{K}$. 3 and 4. The decomposition products, uranyl cyanate, $\text{UO}_2(\text{CNO})_2$, and the double cyanate, $\text{UO}_2(\text{CNO})_3\text{K}$, both golden-yellow in colour. Solutions which are rich in alkaline cyanate contain the potassium salt of a divalent acid, easily dissociated by water:— $[\text{UO}_2(\text{CNO})_4]\text{K}_2$. The dissociation of cobalto cyanates is even greater than that of uranyl cyanate, but becomes about the same when excess of alkaline cyanate is added, which suggests that the two complexes have identical constitutions.

Action of Dimethylamine upon the Two Chloroxyisobutyric Acids and their Derivatives.—E. Fournéau and M. Tiffeneau.—By heating with organic potassium salts the chloro oxyisobutyric ethers are readily transformed into mixed ether salts in which, by the action of thionyl chloride, the hydroxyl can be replaced by an atom of chlorine. By saponification with dilute hydrochloric acid the isomeric chloro-oxyisobutyric acid is obtained. The action of dimethylamine upon these two isomeric acids and their ethers gives the same product. Thus:—



Hence, obviously in I. the atom of hydrogen is not simply replaced by the amine, but the intermediate formation of oxide of ethylene occurs.

Stereo-isomeric Camphane Carbonic Acids.—Ph. Barbier and V. Grignard.—To prepare solid or B pinene hydrochloride, dry hydrochloric acid is saturated with an alcoholic solution of pinene at 75–80°. The liquid hydrochloride distils at 80–82° under 13 mm. Between 84° and 90° under 13 mm. a portion distils which yields a solid hydrochloride. When the hydrochlorides B and A are converted into magnesium derivatives and oxidised, they both yield mixtures of borneol and isoborneol, lævoro-rotatory in both cases, but decidedly more active in the second case than in the first. If the hydrochlorides are converted into acids B gives a dextrorotatory acid fusible at 76–78°. This acid readily isomerises to give a lævo acid fusing at 88–89°. With A a lævo acid fusing at 73–74° is obtained, and as before it isomerises to give a lævo acid of melting-point 86–87°. In spite of the difference of melting-point these two acids are identical. Heating with aromatic amines transforms the acids into their stable isomer. There is complete parallelism between the isomerisation of the camphane carbonic acids and that of the camphols, and like the camphols the α and β acids possess the property of crystallising together in many proportions.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlv., No. 17, 1913.

Influence of Foreign Substances upon the Activity of Catalysts.—C. Paal and M. Windisch.—Of the metals only magnesium and nickel do not influence the power of

platinum of rendering hydrogen active. Aluminium, cobalt, and bismuth very greatly weaken this power, while iron, copper, zinc, silver, tin, and lead remove it altogether. The oxide and carbonate of magnesium also have no effect; lead carbonate behaves like the metal, and the basic nitrate of bismuth makes the platinum almost completely passive.

Active Nitrogen.—Erich Tiede and Emil Domcke.—Strutt stated that the yellow luminescence produced when an electrical discharge occurs in nitrogen is due to the formation of a chemically active modification, and this view was confirmed by Koenig and Elöd. It was supposed that the appearance of the luminescence was due to the conversion of active into ordinary nitrogen. The authors, however, have found that it is not obtained with pure nitrogen, but is dependent upon the presence of oxygen. It is, in fact, a very sensitive test for oxygen in nitrogen.

Atti della Reale Accademia dei Lincei.

Vol. xxii. [ii.], No. 10, 1913.

Palladous Nitrites of Divalent Metals Fixed by means of Organic Bases.—G. Scagliarini and G. B. Rossi.—The extreme solubility of the palladous nitrites of divalent metals makes it impossible to obtain them in the solid state, but hexamethylene tetramine is a convenient reagent for fixing them. By its action compounds of the formula $\text{MePd}(\text{NO}_2)_4 \cdot 8\text{H}_2\text{O} + 2\text{C}_6\text{H}_{12}\text{N}_4$, where $\text{Me} = \text{Mg}$, Mn , Ni , or Co , have been obtained. Of these the compounds of magnesium and manganese are yellow, while those of nickel and cobalt are respectively emerald green and brick-red. The derivatives are isomorphous with one another, and give mixed crystals in all proportions.

MISCELLANEOUS.

Institution of Petroleum Technologists.—Inaugural Meeting, Tuesday, March 3, 8 p.m., at the Royal Society of Arts, John Street, Adelphi. Sir Boverton Redwood, Bart., presiding.

Institute of Metals.—The Annual General Meeting of the Institute of Metals will be held at the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W., on Tuesday and Wednesday, March 17 and 18, 1914. The meeting will commence at 3 p.m. on March 17, and 10.30 a.m. on March 18.

Programme.—Tuesday, March 17: General Meeting of Members in the Hall of the Institution of Mechanical Engineers. Report of the Council on the work of the past year will be presented by the President. The Hon. Treasurer, Prot. T. Turner, M.Sc., will present his Report. The results of the ballots for the Council for 1914 and for the election of new members will be declared. The newly-elected President will deliver his Inaugural Address. The Fifth Annual Dinner of the Institute of Metals at the Criterion, Restaurant, Piccadilly Circus, W., 8 p.m. Wednesday, March 18: General Meeting of Members in the Hall of the Institution of Mechanical Engineers. A selection of Papers will be read and discussed.

Papers.—The following is a list of the Papers and Reports that are expected to be submitted on March 18:—First Report to the Beilby Research Committee, dealing with the solidification of metals from the liquid state, by C. H. Desch, Ph.D., D.Sc.

"Bronze," by J. Dewrance.

"Vanadium in Brass: The Effect of Vanadium on the Constitution of Brass containing 50 to 60 per cent of Copper," by R. J. Dunn, M.Sc., and O. F. Hudson, M.Sc.

"The Quantitative Effect of Rapid Cooling on Binary Alloys" (second Paper), by G. H. Gulliver, B.Sc.

"Crystal Protomorphs and Amorphous Metal," by Prof. A. K. Huntington, A.R.S.M.

First Report of the Nomenclature Committee.

"The Influence of Nickel on some Copper-aluminium Alloys," by Prof. A. A. Read, M.Met., F.I.C., and R. H. Greaves, M.Sc.

"Muntz Metal: The Correlation of Composition, Structure, Heat Treatment, and Mechanical Properties, &c.," by J. E. Stead, D.Sc., D.Met., F.R.S., and H. G. A. Stedman, A.M.I.E.E.

"The Micro chemistry of Corrosion" (Part II.), by S. Whyte, B.Sc., and C. H. Desch, Ph.D., D.Sc.

MEETINGS FOR THE WEEK.

MONDAY, March 2nd.—Royal Society of Arts, 8. (Cantor Lecture).

"Artistic Lithography," by Joseph Pennell.

Royal Institution, 5. General Meeting.

Society of Chemical Industry, 8. "Bleaching of Chemical Pulp, and Suggestions for a Standard Method in Test Cases," by A. Baker and J. Jennison. "Blasting Gelatin, some Notes and Theories," by W. A. Hargreaves. "Application of Calcium Carbide to the Formation of Alloys," by W. R. Hodgkinson.

TUESDAY, 3rd.—Royal Institution, 3. "Modern Ships," by Prof.

Sir John H. Biles, D.Sc., &c.

Royal Society of Arts, 4.30. Discussion on the Paper by Sir Robert W. Perks, Bart., on "The Montreal, Ottawa, and Georgian Bay Canal."

Institution of Petroleum Technologists, 8. "Geometry of the Anticline," by Sir T. H. Holland. "Educational Aims of the Institution of Petroleum Technologists," by E. H. Cunningham-Craig. "Petroleum Technology as a Profession," by Prof. V. B. Lewes.

WEDNESDAY 4th.—Society of Public Analysts, 8. "Composition and

Analysis of Compound Liquorice Powder," by

A. E. Parkes and F. Major. "Composition of the

Saline Matter adhering to certain Wet Salted

Skins," by M. C. Lamb. "Determination of

Carbon Monoxide in Air," by F. S. Sinnatt and

B. J. Cramer. "Suggested Simple Method for the

Approximate Determination of 'Stump'

(Wood) Turpentine in American Gum Turpen-

tine," by L. M. Nash. "Dried Carica Papaya

Juice," by F. F. Shelley.

Royal Society of Arts, 8. "Travels in the Balkan

Peninsula," by H. C. Woods.

THURSDAY, 5th.—Royal Institution, 3. "Heat and Cold," by Prof.

C. F. Jenkin, M.A.

Royal Society. "Action of Light on Chlorophyll,"

by H. Wager. "Formaldehyde as an Oxidation

Product of Chlorophyll Extracts," by C. H.

Warner. "Controlling Influence of Carbon Di-

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THE DISCOVERY OF SIMPLER METHODS OF OBTAINING FORMIC ACID IN QUANTITY.

By F. D. CHATTAWAY.

THE earlier methods of obtaining formic acid ceased to be of any practical importance when Gay Lussac,* in 1831, discovered that it is produced when oxalic acid is heated. He observed that oxalic acid submitted to the action of heat, in part volatilised and in part decomposed, giving a mixture of carbonic acid and an inflammable gas. To ascertain the nature of the latter he put crystallised oxalic acid into a glass retort, and exposed it to a gradually augmented heat. He found that the crystals melted at 98°, and that at 110°, together with the vapour of water, an elastic fluid was disengaged, the amount of which increased as the loss of water of crystallisation allowed the temperature to rise. At 120°-130° the disengagement of gas was extremely rapid, and continued until the acid was completely destroyed. He noted that the gas liberated was a mixture of 6 parts of carbonic acid and 5 parts of carbonic oxide, while in the similar mixture obtained by heating oxalic acid with sulphuric acid equal amounts of the same gases were found. This led him to think that some substance other than water and the oxides of carbon must be formed. On examining the liquid distillate he found it to be acid, and showed that the acidity was due to formic acid.

At first, while the water of crystallisation was being given off, formic acid was only produced in inconsiderable quantity, but more was formed as the decomposition proceeded, and towards the end of the operation when the oxalic acid had become desiccated the distillate had a very penetrating odour and pungent taste.

From the composition of the gas evolved he concluded that 12 parts of oxalic yielded 1 part of formic acid, and noted that the oxalic acid did not sensibly volatilise, but completely decomposed when not too rapidly heated.

This method was so much more simple and convenient than any oxidation method that it soon came into general use, and various improvements in procedure were devised; thus, Gerhardt,† in 1843, says:—"Oxalic acid decomposes into formic acid by heat—it is indeed the best means of preparing the latter; one knows that the employment of sugar or of starch necessitates large apparatus, and never gives a very pure product. I use oxalic acid mixed intimately with very fine sand, and submit the whole to distillation in a glass retort. The operation scarcely needs watching, and the product is very concentrated. It only has to be distilled once in order to free it from any undecomposed oxalic acid. The gas which is disengaged during the operation consists of carbonic acid and carbonic oxide, but the proportion of the latter is not constant, and it appears that it is produced by decomposition of the formic acid."

Other methods of preparing formic acid were soon forthcoming. These we owe, in the first instance, to the extraordinary chemical instinct of Berthelot. Berthelot made a notable discovery in 1855. He shook up ethylene with sulphuric acid, and having diluted the solution with water distilled it, thus synthesising alcohol. This conversion of ethylene into alcohol led Berthelot to another and more important discovery.

It had long been known that ethyl alcohol when heated with sulphuric acid yields ethylene and water, while formic acid similarly heated with sulphuric acid yields

carbonic oxide and water. He argued that since the former process could be reversed the latter might also. This, in a sense, he succeeded in effecting* by allowing carbon monoxide to act on potash at a raised temperature. He placed 10 grms. of damp potash in a half litre flask filled with carbon monoxide, sealed it up, and heated it in a water-bath for seventy two hours. When the flask was opened under mercury the gas was found to have been completely absorbed, and on dissolving the solid product in water, acidifying with dilute sulphuric acid, and distilling, formic acid was obtained.

Berthelot did not work out the details of this process or suggest its use as a method of preparing formic acid. This was done nearly forty years later by Merz and Tirbirica.† During the last twenty years it has become the technical method of manufacturing formic acid, which has, in consequence, become so cheap that it is now extensively used.

Berthelot almost at the same time discovered a second method of making formic acid, which, until it was manufactured on a large scale from carbon monoxide, was almost exclusively used, and is still the most convenient laboratory method.‡

During the years 1853-1854 Berthelot was engaged in studying the action of acids upon glycerol, and one can hardly doubt that in the course of this investigation he heated among others oxalic acid with glycerol. It was thus chance rather than the deliberate attempt to find a method of combining carbonic acid in the nascent state with water, which he advances in his paper, that led him to the discovery that formic acid is thereby produced.

Berthelot found§ that when oxalic acid, glycerol, and a little water were heated together for from twelve to fifteen hours at 100° C. practically half the carbon of the oxalic acid escaped as carbon dioxide, and that the remaining half could be obtained as formic acid by distilling the residue with water. He regarded the glycerol simply as furthering by contact the decomposition of the oxalic acid, and considered that after the evolution of the carbon dioxide the formic acid remained dissolved in the glycerol "as ammonia in water."

Berthelot's method of obtaining the formic acid by distilling the residue repeatedly with water was inconvenient and tedious, and was soon replaced by the familiar continuous process which was worked out in great detail by Lorin, at first in Berthelot's laboratory.¶ The common method of preparing allyl alcohol from glycerol is an indirect consequence of Berthelot's work, as it was discovered by Tollens when preparing formic acid by Lorin's method. He did not at first properly regulate the heat, and obtained a product of extraordinarily pungent smell which violently attacked the eyes. From the distillate a liquid not miscible with water was separated which proved to be allyl formate. Subsequent work showed that allyl alcohol was produced in large quantity when oxalic acid and glycerol were rapidly heated together to the temperature at which the evolution of CO₂ again became vigorous after having markedly slackened.

It is a curious circumstance that only within the last few months has a satisfactory explanation of the course of these reactions been put forward.

That given in different text books varies somewhat, but, speaking generally, the statement is made that at about 100° C. the oxalic acid decomposes into carbon dioxide and formic acid, the latter then reacting with the glycerol to

* *Comptes Rendus*, 1856, xli., 955; *Ann.*, 1856, xcvi., 125.

† *Ber.*, 1880, xlii., 23.

‡ Kolbe and Schmitt's synthesis (*Annalen*, 1861, cxix., 251) of formic acid from carbon dioxide may be referred to here. They state that the action goes very easily, and express surprise that it has not long ago been observed. Metallic potassium in thin shavings was placed on a shallow dish over water under a bell-jar, and carbonic acid was continuously led in. After twenty-four hours the metal was found to be converted into a mixture of potassium bicarbonate and potassium formate.

§ *Comptes Rendus*, lii., 447; *Ann.*, 1856, xcvi., 139.

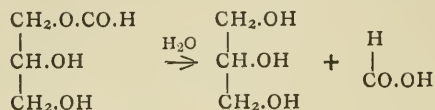
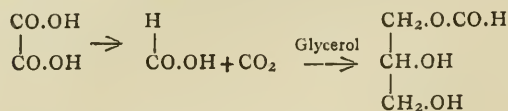
¶ *Bull. Soc. Chim.*, 1866, [2], v., 7.

• *Zeitschrift für Chemie*, 1866, li., 513.

* *Ann. Chim. Phys.*, 1831, xli., 218.

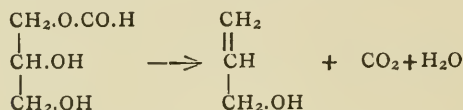
† *Ann. Chim. Phys.*, 1843, [3], vii., 129.

produce monoformin. This, on the addition of a further quantity of the crystallised acid, is hydrolysed by the water of crystallisation which is given off, the formic acid liberated distilling over while the oxalic acid left decomposes as before, yielding formic acid which in its turn reacts with the regenerated glycerol, thus:—



this cycle of operations being capable of repetition as often as desired.

The production of allyl alcohol when a mixture of oxalic acid and glycerol is rapidly heated to about 250° is invariably stated to be due to a decomposition which the monoformin produced as above undergoes, whereby it splits up into allyl alcohol, carbon dioxide, and water, thus:—

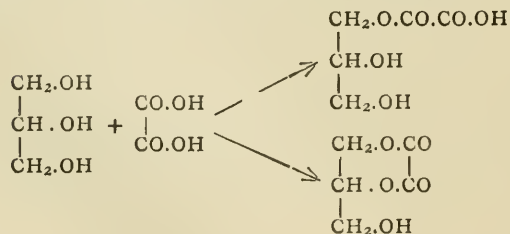


These explanations are fundamentally incorrect. A moment's consideration suggests that the first reaction is unlikely to be a decomposition of oxalic acid into formic acid and carbon dioxide, since oxalic acid does not decompose to any appreciable extent until a temperature is reached much above anything ever recommended in the method under discussion.

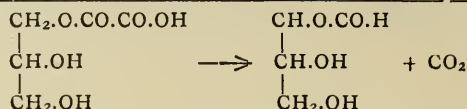
That the second assumed reaction, the decomposition of the monoformin by the water of crystallisation liberated when the further amount of crystallised oxalic acid is added, is not the main source of the formic acid which distils over, is shown by the well known fact that neither water nor crystallised acid need be used, since, if anhydrous oxalic acid is added, a distillate containing over 98 per cent of formic acid can easily be obtained.

That some compound must be formed before carbon dioxide makes its appearance is clear, since, while other polyhydric alcohols may be used in place of glycerol, the temperature at which the evolution of gas begins to be rapid varies considerably, depends upon the alcohol employed, and is not within narrow limits the same, as it would be were the oxalic acid itself decomposing.

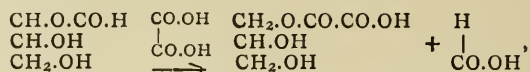
The true explanation* is the obvious one. The oxalic acid reacts with glycerol† as it does with other alcohols, both an acid and a normal oxalate being produced.



The former like all such compounds is unstable at a slightly elevated temperature, and decomposes when this is reached into carbon dioxide and monoformin, thus:—



The oxalic acid added displaces the formic acid from the monoformin, thus:—



and the cycle of operations is then repeated.

That this is the correct explanation is shown by the observation that glycerol and oxalic acid interact readily at a temperature below that at which carbon dioxide begins to be evolved, and that, although the acid oxalate which must be formed has not yet been isolated, the products of its interaction with aniline and with ammonia, oxanilic acid and oxamic acid respectively, have been obtained.

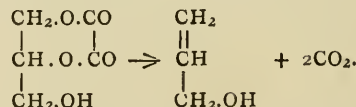
That the whole course of the reaction is as above formulated is rendered practically certain by the fact that a precisely similar cycle of operations can be carried out with ethyl alcohol and oxalic acid when the products can easily be isolated at every stage.

As is well known, ethyl-hydrogen-oxalate, which is formed when ethyl alcohol and oxalic acid are heated together and which can be distilled under diminished pressure, decomposes into carbon dioxide and ethyl formate when heated under ordinary atmospheric pressure, this being the source of the ethyl formate always obtained in such quantity in the ordinary preparation of ethyl oxalate, when the product of heating together oxalic acid and ethyl alcohol is distilled. Oxalic acid heated with ethyl formate displaces the formic acid, producing ethyl hydrogen oxalate.

The more complicated reaction which goes on when glycerol and oxalic acid are rapidly heated together until evolution of carbon dioxide practically ceases, and then at a much higher temperature recommences, and which is always employed for the preparation of allyl alcohol, takes a course which also might have been predicted.

It is possible, though it seems unlikely, that monoformin can decompose to a very limited extent as stated in the text-books, but the chief, if not the sole, source of the allyl alcohol is the normal oxalic ester, dioxalin.

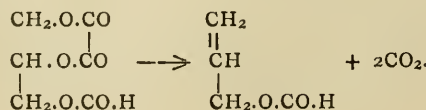
$\text{CH}_2\text{O.CO.CO.OH}$, which, on heating, splits up into carbon dioxide and allyl alcohol, thus:—



The presence of this compound in the reaction mixture, after the first evolution of carbon dioxide has ceased, is shown by the production of oxamide or oxanilide when ammonia or aniline is added; these compounds being only thus producible from such a normal ester.

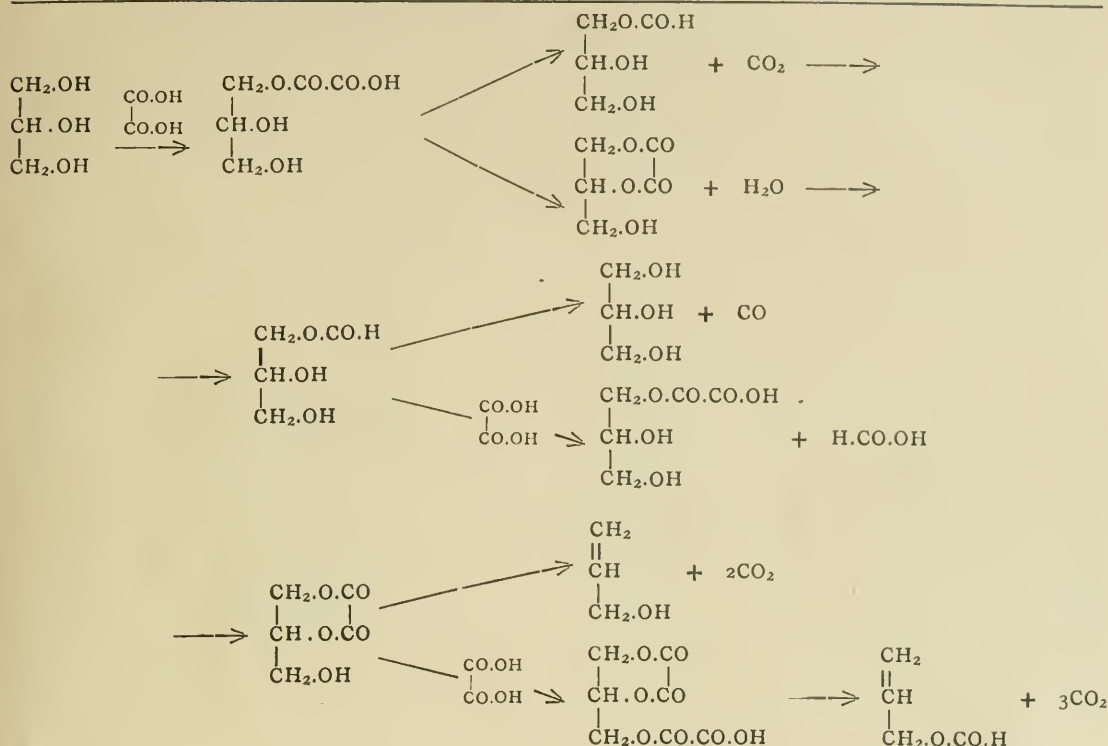
As the quantity of oxamide obtainable always corresponds within the limits of experimental error with the amount of allyl alcohol obtainable, the correctness of this theory of the process is established.

The allyl formate, a little of which is always obtained when allyl alcohol is thus prepared, results from a similar decomposition of oxal-formin, which is produced from monoformin or dioxalin by the further action of oxalic acid, thus:—



* *Trans. Chem. Soc.*, 1914, cv., 151.

† Either the α- or the β-hydroxyl group may interact. To save space only the equations relating to the former are given here.



The small amount of acrolein and the large quantity of carbon monoxide, which are also formed as by-products in the reaction, result from the decomposition by heat of glycerol and monoformin respectively, the latter yielding carbon monoxide and glycerol, just as formic acid yields water and carbon monoxide when heated.

The main reactions, which take place when glycerol and oxalic acid are heated together, should therefore be formulated as shown in the accompanying scheme.

THE RELATION OF PASSIVITY TO THE PHENOMENON OF ELECTROLYTIC VALVE ACTION.*

By Dr. GÜNTHER SCHULZE,
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PASSIVITY and electrolytic valve action seem to be the most complicated and most difficult of explanation of all anodic phenomena. Many relations between them will be shown best by reviewing the most important features of both.

To begin with electrolytic valve action, we must differentiate between two varieties of it, ionic and the electronic valve action, the latter of which may be further divided into direct-current valve action and alternating-current valve action.

Silver in an aqueous solution of HBr gives an example of ionic valve action. If a current of 3 $\frac{\text{milliamp.}}{\text{cm.}^2}$ is passed through an anode of silver in this solution a smooth black layer is formed on the silver that grows proportional to the amount of electricity passed. After some time the colour of this layer turns to an olive-green. The forma-

tion of the layer is accompanied by a proportional rise of the electric tension across it. After a formation of some days with a current of 3 $\frac{\text{milliamp.}}{\text{cm.}^2}$ the layer attained a thickness of 0.85 millimetre, and supported a tension of 400 volts at a current density of 0.2 $\frac{\text{milliamp.}}{\text{cm.}^2}$.

The most striking phenomenon of ionic valve action, however, by which it is distinguished both from the electronic valve action and passivity, is that no gas is developed at the anode. The whole amount of current is absorbed in the formation of the solid layer. By increasing the current density it is possible to disrupt the layer, after which all the current passes through the damaged spot and gives rise to a continuous stream of gas bubbles for hours or even days, while the tension at the layer is greatly lowered. But this development of gas is only an apparent exception to the given phenomenon, as it interrupts the formation.

If the current through a formed silver anode is reversed valve action appears. The tension, high at the first moment, drops almost instantaneously to a low value. If the original direction of the current is restored the tension is low at first, but regains its former amount very quickly. These changes of tension, however, are quite unable to follow the oscillations of an alternating current of 50 periods a second, and in consequence there is not the slightest sign of rectification of such a current by a silver anode in hydrobromic acid.

It is easily understood that all these phenomena are caused by the various resistances the different ions find in the layer of silver bromide. As the time the ions take to pass the layer is large compared to 0.01 second, ordinary alternating current cannot be rectified.

Ionic valve action occurs further with silver in HCl and HI and with copper in HF.

Electronic valve action shows quite different and much more intricate features. Aluminium, the first valve metal known, may serve as a first instance for their description.

* A Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, November 12, 1913.

If aluminium in a suitable electrolyte, such as a solution of $\text{Na}_2\text{B}_4\text{O}_7$, is made the anode of a constant direct current, there is both oxygen developed and a solid skin of aluminium oxide formed at its surface. At first this solid skin is so extremely thin that it is invisible. After some time it appears as a whitish-grey film of a hard, almost crystalline structure that is pierced by innumerable pores of microscopic size. The formation of this solid film absorbs only about 5 per cent of the whole current available. The rest of it develops free oxygen that escapes.

Thus the valve metals show quite the same strange phenomenon as the passive metals, viz., anodic rise of oxygen from a metal that combines with it very readily in the ordinary state.

Taking H_2SO_4 as electrolyte we find this still more obivous. Iron as well as aluminium form easily soluble compounds with it, whereas when used as anodes and loaded with a sufficient current density neither dissolve, but oxygen is set free at their surface. In the case of aluminium the phenomenon is still more puzzling than with iron, as aluminium combines very violently with oxygen. In air it only seems to be inactive because it protects itself from the oxygen by a continuous, impermeable skin of aluminium oxide, which momentarily covers every scratch made on an aluminium surface and is at first of little more than molecular thickness. By diffusion of oxygen through it, it grows very slowly. When its formation is made impossible, as by amalgamating the aluminium with mercury, a stormy reaction of the aluminium with the oxygen of the air takes place at once, and strangely shaped dendrites of aluminium oxide grow quickly and steadily out of the amalgamated surface. And for all that even nascent oxygen is set free from aluminium surfaces in H_2SO_4 .

Before we try to explain this fact we must lay stress upon the most important difference between passive metals and valve metals. It is still open to discussion whether passivity is caused by a layer of oxide or not, but if there is such a layer it possesses metallic or electronic conductivity. Thus it serves as an anode instead of the metal it covers, and there is no reason why it should grow much beyond molecular thickness.

The oxide skin on the valve metals, on the contrary, insulates very perfectly. In consequence it cannot serve as an anode, but only as an obstacle that is constantly pierced by the ions and constantly regenerated by chemical action. Thus the film grows proportional to the time the current is flowing and gives rise to the following various phenomena which are completely absent from passive anodes.

The first is the rise of tension at the valve anode, that is also proportional to the time of formation until it reaches a well defined point, at which innumerable fine sparks become visible at the anode. This point is called sparking voltage. Beyond it the tension decreases to a second definite value, the maximum voltage, which, with a given combination of valve metal and electrolyte, cannot be exceeded. If, on the other hand, not the current but the tension is kept constant at a value that lies below the maximum voltage, the current continually decreases and soon reaches extremely small values. Then the "effective layer" upon the anode has a resistance of many megohms and may be regarded as the dielectric of an electrostatic condenser, whose electrodes are formed by the valve metal on one and the electrolyte on the other side. The capacity of this condenser is easily measured and found surprisingly large. Furthermore, it is almost inversely proportional to the tension at which the valve metal is formed independent of the nature and concentration of the electrolyte used, at long as aqueous solutions are employed. For each valve metal, however, and every non-aqueous solvent it has a different characteristic value. One square centimetre of an aluminium anode formed at 100 volts in an aqueous solution has a capacity of 0.08 microfarad. From this capacity the thickness δ of the effective layer

might be calculated if the dielectric constant ϵ of this layer were known. As it has not been possible yet to measure it, we must be content to calculate the relative or reduced thickness δ/ϵ by simply assuming $\epsilon = 1$. According to the behaviour of the capacity of the effective layer stated above its thickness δ/ϵ is nearly proportional to the forming voltage and a characteristic function of each valve metal. The reduced thickness of the effective layer upon an aluminium anode formed at 100 volts in an aqueous solution amounts to 0.000010 millimetre.

At first sight it might be supposed that "effective layer" and solid oxide skin were identical, but a research as to the thickness of the latter shows that this supposition is wrong. As the oxide film is much too thin to ascertain its thickness mechanically, it must be measured in the same way as the effective layer, viz., by measuring its electrostatic capacity. The oxide film must be made the dielectric of a condenser. For this purpose it is carefully rinsed with distilled water in order to free it from the last traces of the electrolyte and carefully dried, whereupon the cell is filled with mercury instead of the electrolyte. Thus we have a condenser whose conductors are aluminium and mercury, and whose dielectric is formed by the whole thickness of oxide film. By measurements of this kind it was found that the effective layer which causes all the phenomena of the valve action and the solid oxide film are entirely different phenomena, which must be sharply distinguished. While, as stated above, the thickness of the effective layer of a given valve metal is only dependent on the forming voltage as long as aqueous solutions are used, the thickness of the solid oxide film is not always much larger than that of the effective layer, but depends also on the nature and concentration of the electrolyte and its temperature, the density of the forming current, and may even in certain cases grow continuously, while forming voltage and thickness of the effective layer are maintained at a constant value. Thus the effective layer must be something essentially different from the oxide film, and it is hardly imaginable that it can be anything else but a gas layer within the microscopic pores of the solid film.

Thus I was led to adopt the following view of the different layers at a formed valve metal's surface and of the processes which originate it.

δ' in Fig. 1, which gives a greatly magnified diagrammatic scheme of the layers, is the whole of the solid oxide skin and consists of the following parts:—

1. α , the continuous oxide skin of molecular thickness that always covers aluminium surfaces.

2. β , the gas layer within the pores of the porous oxide film.

$\alpha + \beta = \delta$ is the "effective layer." As α is very small relative to β it may be neglected and δ simply be called the gas layer.

3. γ , the part of the solid porous film whose pores are filled with the electrolyte. Its resistance is a good deal larger than that of the electrolyte, but may be neglected when compared with the resistance of the gas layer.

These different layers seem to arise in the following way. If a newly polished aluminium anode is immersed in the electrolyte, it is covered with the layer α , which insulates, but for its molecular thickness can withstand only very small tensions. It is obvious that as soon as the current is closed the layer α will be pierced everywhere by the incoming ions, or rather an easily derivable part of them, the oxygen. The oxygen ions having passed the layer and reached the aluminium transfer their charge to it and form a new oxide film below the original, which is disrupted again by new ions, thus forming a thicker porous oxide skin.

But how does the gas layer form, and why does the greater part of the oxygen escape?

The only possible explanation of this seems to be the assumption that most of the oxygen ions do not reach the aluminium itself but give up their charge, the negative electrons, when they encounter an obstacle of high

resistance and in consequence a high potential gradient, and that the freed electrons only pierce the resisting layer.

The places at which the oxygen ions encounter an extremely high resistance are the junction between gas layer and electrolyte as well as the junction between gas layer and the solid continuous film α . Let us suppose that the greater part of the oxygen ions lose their electrons when they arrive at the junction between electrolyte and gas layer. The electrons fly to the aluminium and the neutralised oxygen atoms escape out of the oxide skin, as they get a heavy impact by their separation from the electrons. The small number of oxygen ions which did not give up their electrons at that limit, because it just was in an oscillatory state that prevented the electrons from escaping, passes the gas layer and arrives at the second junction between the gas layer and the solid film α . Here the same will happen as

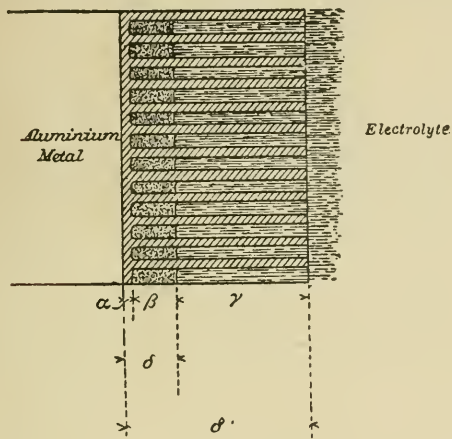


FIG. 1.

at the first junction. Most of the ions will lose their electrons, a few, prevented from doing so by their momentary (oscillatory) state, will pierce the solid film α , oxidise the aluminium, and reinforce the oxide film. The oxygen ions which are neutralised at this second limit cannot escape, but cause the growth of the gas layer.

It would lead us too far to show how all phenomena of valve action can be explained by means of this scheme.

Another classification of valve action, which has its analogy in passivity, is that of complete and incomplete valve action. When a valve metal is insoluble in the electrolyte it shows complete valve action. Tantalum behaves like that in almost all electrolytes. In contrast to it the valve action becomes more incomplete the more the valve metal is soluble in the electrolyte. Aluminium shows many instances of it. The characteristics of incomplete valve action are:—The forming current does not converge to zero when the voltage is kept constant, but to a constant value, which is higher the more the valve metal is soluble. The maximum voltage cannot be reached, but the formation stops at a lower voltage. Aluminium in dilute sulphuric acid, e.g., can only be formed at 20 volts instead of 400, which would be reached if the valve action were complete. The forming current must exceed a minimum value before formation sets in. After breaking the current the valve action disappears again.

Most of these features are also shown by iron becoming passive in dilute sulphuric acid; a marked solubility, a minimum current for starting the passivity, its disappearing after breaking the current. On the contrary, iron in concentrated HNO_3 shows complete passivity.

The performance of the valve metals as cathodes is best seen by taking oscillograms of the alternating current and voltage applied to a valve cell. As mentioned before, we

must distinguish between direct-current valve action and alternating-current valve action. To which of these a cell belongs does not depend on the valve metal only but also on the electrolyte. The combinations with direct-current valve action show all the described phenomena as long as the valve metal remains anode, but the moment the current is reversed the valve action is destroyed and the cell must be re-formed from the beginning, when the valve metal is made the anode again. Alternating current is not rectified, but passes the cell unhampered in both directions.

Combinations with alternating current valve action rectify alternating-currents up to the highest frequencies. Between both there are many intermediate states. Bismuth, antimony, cadmium, and zinc are valve metals which show d.c. valve action in aqueous solutions. The reason is obvious. Their oxide films are reduced by the cathodic hydrogen. In pure sulphuric acid they rectify alternating currents, as the skin formed in this electrolyte seems to consist of the sulphate instead of the oxide and is not reduced by the hydrogen.

Here we find another relation to the behaviour of passive metals. Their passivity is also destroyed by hydrogen developed on them in the cathodic direction of the current. But this seems to be the case with all passive metals. The analogy to alternating-current valve action is missing; no passive metal combines so vigorously with oxygen that the compound may withstand reduction. This may be explained by the fact that if the oxide-film theory is correct, tantalum, the *non plus ultra* of alternating-current valve action, is unable to rectify alternating currents in solutions of AuCl_3 and PdCl_2 , as the current in its cathodic direction deposits gold or palladium at the tantalum. To dissolve it again the same amount of electricity is wanted in the anodic direction, and the valve action is made ineffective. Other cations are only partly deposited, so that a part of the valve action survives. Fig. 2 shows this clearly. It is an oscillogram of an alternating current and voltage of the frequency 50 applied to tantalum in an aqueous solution of $\text{Cu}(\text{NO}_3)_2$, 0.2 normal; a is the current through the cell, b the tension at its connections. The surface of the tantalum was 2 cm.².

At the point o the tantalum becomes cathode. The current remains zero until the voltage has reached the point c ; also in the cathodic direction there is a minimum potential that must be surpassed before the current through the effective layer can start. While it flows and deposits copper on the tantalum the voltage is almost constant at first, and decreases to zero, together with the current thereafter. At d the tantalum becomes anode; but as there is copper deposited on it, it behaves like an ordinary copper anode up to the point e , where the current suddenly drops to nearly zero and the voltage rises to its normal valve value. It is obvious that when the current has reached the point c all the copper deposited before on the tantalum has been consumed and the valve action is re-established. Thus only a part of the current flowing in the cathodic direction has deposited effective copper; the rest must have developed hydrogen or deposited copper in a state in which it could not serve as anode. The cations Cd, Ag, Zn, Pb, Fe, Tl act in the same way with decreasing effect along the row. With all other cations, especially with Bi, Hg, Cr, Mn, Co, Ni, tantalum shows undisturbed alternating valve action, for which the oscillogram Fig. 3 may serve as a paradigm. It was taken from a cell with tantalum in an aqueous solution of KNO_3 , 0.5 normal.

V is the voltage of the open circuit. The other points are easily understood on account of their likeness to Fig. 2.

The only phenomenon I want to lay stress upon is that the current a becomes zero at d , that is, before the voltage has disappeared. That proves that there is also a minimum potential below which the current cannot subsist, analogous to the electric arc for instance.

In the anodic direction the current through the cell is zero from the beginning. The small current shown in Fig. 3 does not pass the effective layer, but is the charging current of the high electrostatic capacity of the layer, as is

sufficiently shown by the fact that it is shifted through 90 degrees against the voltage.

This phenomenon, that the current is zero from the beginning, is important for the theory of valve action. If valve action were caused by a partial destruction of the oxide film in the cathodic direction and a reforming of it in the anodic, as some authors formerly held, or by some kind of diffusion different in both directions, there must at all events be a re-forming current through the cell in the beginning of each anodic period. That there is none is a conclusive proof for the supposition that the effective layer is not changed by the cathodic direction of the current and that valve action cannot be explained by diffusion—in short, that it is not an ionic but an electronic phenomenon.

Summarising the essentials of valve action from the statements above we may say:—There is a defined high anodic and a defined low cathodic voltage, which must be

dissolve chemically in acids and anodically in electrolytes, behave differently in some cases. When dipped in certain strong acids they do not dissolve, and when made anodes in corresponding electrolytes they develop oxygen instead of forming ions. Some of them are passive in all electrolytes, others only in some cases. The latter may be subdivided into those which are passive without the aid of an anodic current and those which turn from the active into the passive state only when the anodic current is strong enough. Iron in dilute HNO_3 or H_2SO_4 is an instance of the last type. When the iron has entered the passive state the current may be lowered a good deal below the amount at which the passivity arose before the ions become active again. Increasing temperature decreases the passivity, cathodic hydrogen destroys it.

Some authors have found that passive anodes possess a very great electrostatic capacity, and have concluded that they were covered by an oxide film. Other authors have

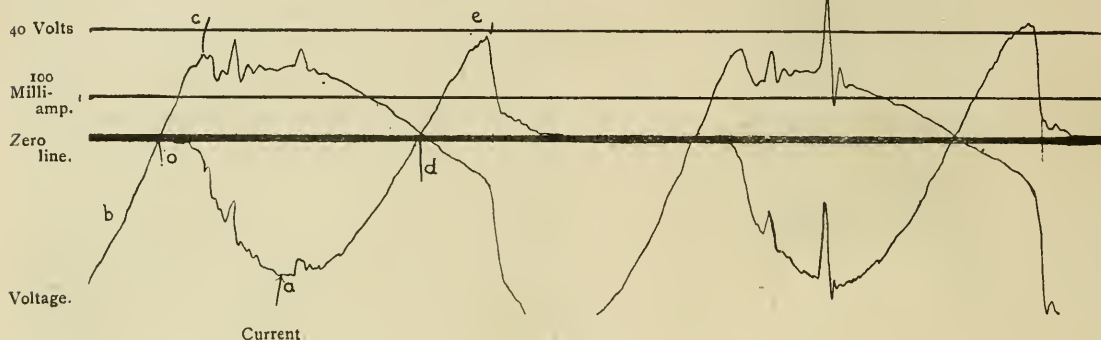


FIG. 2.

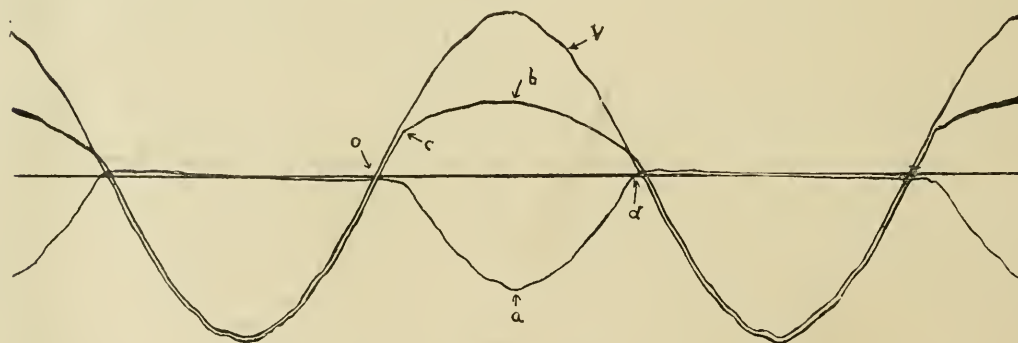


FIG. 3.

exceeded before a current can flow through a valve electrode. The first is identical with the voltage at which the valve metal is formed, the second is the "minimum potential."

That the anodic voltage is high was explained above by the assumption that electrolytic anions must be subjected to a high potential gradient ere they lose their electrons, which in this case are bound to non-metallic atoms. In the same way the low cathodic voltage may be explained by the supposition that a relatively low potential gradient suffices to free the electrons from the valve metal. Thus the electronic valve action is caused by the different forces with which the non-metallic (electronegative) atoms and metallic (electropositive) ions bind the electrons.

The phenomena of passivity have been partly mentioned in the above. In the following only the most important of them will be summarised. Some metals which would be expected according to their position in the electrochemical series and to their general chemical behaviour to

put forward more reasons for such a film, but its existence did not remain unquestioned.

As I have not worked myself on passivity it is not for me to take a part in this controversy. The only thing I wish to point out is the remarkable analogy between the phenomena of valve action and passivity which follows from the assumption that valve action is caused by an insulating film and consequently a gas layer, while passivity takes place if the film shows metallic (electronic) conductivity together with a limited or negligible solubility in the electrolyte.

The consequence of the metallic conductivity of the film is that it cannot grow much above molecular size and must be almost undetectable by optical or mechanical means. The oxygen developed at its outer surface covers it more or less and protects it against the electrolyte when it has been formed. Thus the current may be decreased below the critical forming value without restoring activity.

The behaviour of iron in H_2SO_4 of different concentra-

tion is of special interest. In dilute sulphuric acid it shows passivity, in concentrated acid valve action. In intermediate concentrations an unstable valve action is succeeded by stable passivity. In dilute solutions the anion SO_4 may form an oxide of iron by the aid of the water. In concentrated solutions the small amount of water present is not available for this reaction, as it is bound to the sulphuric acid itself. Therefore ferric sulphate must be formed. This insulates and causes valve action.

Therefore I hold:—Valve action is caused by an insulating skin of ultra molecular thickness with a thin gas layer within it; passivity by a conducting skin of molecular thickness with a molecular gas layer upon it.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

DISEASE OF TIN.

Very curious researches on the density of tin at different temperatures have recently been made by M. Pascal. They have been communicated to the Academy of Sciences by M. Henry Le Châtelier. In a solid state tin possesses three allotropic varieties; in a liquid state it presents an allotropic variety like sulphur. The disease or pest of tin, as it has been called by the learned Dutchman Ernst Kohen, seems to be constituted by one of these allotropic varieties. This sick tin, spotted with grey pulverulent spots, has a density inferior to about 15 per cent to that of normal tin. The metal has undergone, as it were, a swelling followed by a molecular disaggregation. The third allotropic variety is distinguished by a somewhat different crystalline structure.

NEON TUBES AND THE AURORA BOREALIS.

The origin of the Aurora Borealis still remains mysterious; nevertheless, a very ingenious explanation has just been given to the Academy of Sciences by M. George Claude in a paper presented by Prof. d'Arsonval. M. Claude has noticed that the difference of potential at the limits of neon tubes decreases to a half, third, or quarter of the ordinary value when the diameter of the tube doubles, triples, and quadruples, so that very small voltages would suffice to work enormous tubes. Besides the practical consequences of such a state of things from a lighting point of view, this observation, as Prof. d'Arsonval suggests, brings with it the explanation of one of the most interesting physical problems of the globe. If, indeed, the results of M. Claude are applicable to other gases of the globe, the magnificent Aurora Borealis, which are but the electrical discharges of nebulous action, would only require differences of potential far inferior to what might be thought necessary and the existence of which was difficult to understand.

GRADUAL COOLING OF THE EARTH.

M. Appel, President of the Academy of Sciences, at the last sitting of the assembly, presented an important work by M. Verona on the gradual cooling of the earth. At the same sitting M. Andrade presented a paper on a new method of compensation of chronometrical apparatus. M. Roux, director of the Pasteur Institute, also made a new communication from MM. Fillat and Jouassier concerning the training of microbes in suspension in water under the influence of a draught. These authors have already shown that the superficial tension of the liquid has a more or less great influence on this action. Their recent works show that the nature of the microbe and its age likewise have an influence on the evolution of the phenomenon.

RÔLE OF INSECTS IN THE TRANSMISSION OF DISEASES.

Numerous diseases are transmitted by stinging insects. This is the case for yellow fever, which is spread by the

stegomyia; the sleeping sickness, also, is propagated by the *tse-tse* flies, &c. But besides these mosquitoes and flies, fleas would seem to play a very important rôle in the propagation of the deadly diseases. Experimental researches have just been made at the Pasteur Institute on the part played by these insects in trypanosomiasis. Their rôle is henceforth distinctly determined. The fleas that bite infected animals are contaminated, and in their turn they transport the microbial agent on to other animals that they may happen to sting.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 19, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

By invitation of the President, Prof. MAX WOLF exhibited a series of slides of Nebulæ, from the Observatory of Heidelberg.

Papers were read as follows:—

"*The Brain of Primitive Man, with Special Reference to the Cranial Cast and Skull of Eoanthropus* ('the Piltdown Man')." By Prof. G. ELLIOT SMITH, F.R.S.

An account is given of the difficulties that present themselves in any attempt to reconstruct "the Piltdown skull" from the few damaged fragments that have been recovered, and attention is called to a large series of points of anatomical detail which indicate the only way in which these difficulties can satisfactorily be circumvented.

The cranial cast obtained when thus correctly reconstructed is compared with those obtained from the calvaria of *Pithecanthropus*; the Mousterian series of crania (especially those found at Neanderthal, Gibraltar, La Chapelle aux-Saints, and La Quina); those representing Auragnacian and later times; and a number of cranial casts and actual brains of primitive types of modern men and apes.

The results go to prove that the small brain of *Eoanthropus*, though definitely human in its characters, represents a more primitive and generalised type than that of the genus *Homo*. Nevertheless, it can be regarded as a very close approximation to the kind of brain possessed by the earliest representatives of the real *Homo*, and as the type from which the brains of the different primitive kinds of men—Mousterian, Tasmanian (and Australian), Bushman, Negro, &c., no less than those of the other modern human races have been derived, as the result of more or less well-defined specialisations in varying directions.

From the features of its brain *Pithecanthropus* must be included in the family Hominidæ, but it and *Eoanthropus* can be looked upon as divergent specialisations of the original genus of the family. *Pithecanthropus* represents the unprogressive branch which survived into Pleistocene times before it became extinct; *Eoanthropus* the progressive phylum from which the genus *Homo* was derived.

Special attention is devoted to the study of the temporal region of the brain, which in all of these fossil men (not excluding *Pithecanthropus*) reveals features of great morphological interest. The opinion is expressed that the increased size of the brain (as a whole) which is distinctive of the Hominidæ, among the Primates, is intimately related to the acquisition of the power of articulate speech, and that the very earliest representatives of the family must have possessed in some slight degree the definite faculty of inter-communication one with another by means of vocal sounds. The development of asymmetry of the brain was necessarily incidental to the acquisition of human characteristics, and must have been already present in the original Hominidæ.

"Oxidases." By Prof. A. J. EWART.

"New Malarial Parasite of Man." By J. W. W. STEPHENS, M.D.

"Investigations Dealing with the Phenomena of 'Clot' Formations. Part II. The Formation of a Gel from Cholate Solutions having many Properties Analogous to those of Cell Membranes." By S. B. SCHRYVER.

"Influence of the Position of the Cut upon Regeneration in *Gunda ulvæ*." By DOROTHY JORDAN LLOYD, B.Sc.

CHEMICAL SOCIETY.

Ordinary Meeting, February 5, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 104).

37. "A Criticism of Holmes' Method of Determining the Molecular Complexity of Liquids." By WILLIAM ERNEST STEPHEN TURNER.

In a recent paper (*Trans.*, 1913, clii., 2147), and in continuation of previous work (*Trans.*, 1906, lxxxix., 781; Holmes and Sageman, *Trans.*, 1907, xci., 1608; 1909, xcv., 1919), Holmes sets out the results of a method which he employs for the determination of the molecular complexity in the liquid state. As a new method of attacking an old problem it deserves a welcome, but the results are so much different from those deduced on the basis of other and well-known methods that they call for examination.

The view adopted by the author of the theory is that in most cases the only forces which are brought into action when two liquids mix are of a physical character, and that the miscibility of liquids depends on the true relative molecular volumes, or what comes to the same thing, the relative radii, of the constituents. The method employed to obtain the relative complexities is, therefore, to determine the molecular composition, referred to the gaseous state, of the liquid mixture in which the maximum deviation occurs between the calculated and observed proportions by volume of the constituent with the larger molecular volume. The ratio of the molecular proportions so obtained is considered as that of the relative molecular complexities, water, for example, from its mixture with ethyl tartrate being considered to have a molecule, $(\text{H}_2\text{O})_4$, relative to the ester; and by similar processes, molecular formulæ $(\text{C}_4\text{H}_{10}\text{O})_4$, $(\text{CHCl}_3)_8$, $(\text{C}_6\text{H}_6)_8$, $(\text{C}_6\text{H}_{14})_8$, and $(\text{CS}_2)_{16}$ are assigned. In practice, however, the method is not so simple as it appears; thus, the mixtures of maximum deviation in the case of water with ethyl and propyl alcohols are $\text{C}_2\text{H}_5\text{O} \cdot 1\frac{1}{4}\text{H}_2\text{O}$ and $\text{C}_3\text{H}_7\text{O} \cdot 1\frac{1}{4}\text{H}_2\text{O}$ respectively, and of water and *n*-butyric acid, $\text{C}_4\text{H}_8\text{O}_2 \cdot 7\text{H}_2\text{O}$; yet the alcohols and butyric acid are nevertheless held to be of a similar complexity to water in order to agree with the author's theory that molecular radii must have certain values to permit of miscibility. Nor are substances of approximately equal molecular volume, like aniline and ethyl acetate, soluble in water to anything like the same extent, and to explain this discrepancy, speculations are introduced concerning the quasi-electrical forces which are presumed to act, causing disturbances in the molecular volume or co-volume.

Without dealing further with these speculations, however, it may be said that the results themselves are sufficient evidence of the antagonism between this method and those based on current physico-chemical doctrines. The main points to be noted about the values of the degree of complexity given by Holmes are that (1) they appear to vary from substance to substance by the factor 2, being 1, 4, 8, or 16; (2) they are represented by integral numbers; (3) the substances which all others methods demonstrate to be normal are often the most associated of all.

Now the occurrence of whole numbers as association factors must have a definite meaning. In a gas the mole-

cules of which are capable of association there is at any temperature a condition of equilibrium between two sets, the more and the less complex molecules, this equilibrium being readjusted at each alteration of temperature. With sulphur vapour, according to the conditions of temperature and pressure, molecules S_8 , S_6 , S_2 , and S_1 exist, three forms often co-existing (Preuner and Schupp, *Zeit. Phys. Chem.*, 1909, lxxviii., 129). There is no *a priori* reason to suppose that in the liquid state an associated substance can have but one degree of complexity independent of temperature; indeed, it would be surprising if the general effect of temperature and pressure was entirely different for different states of matter. The case of nitrogen peroxide may be quoted against such a possibility; for as liquid nitrogen peroxide becomes coloured with rise of temperature, it must of necessity indicate that a different molecule is being produced, almost certainly NO_2 , since the substance of this formula has a brown colour in the state of vapour; thus, without any assumption either as to the distribution of kinetic energy added to a substance, or of the actual molecular complexity, the behaviour of nitrogen peroxide clearly shows that the degree of aggregation of a liquid is certainly affected by temperature variation. If Holmes's theory is correct, however, then it is most improbable that temperature has such an effect. Holmes himself admits this (*Trans.*, 1913, clii., 2164), for if the degree of complexity can be represented as a whole number in every one of the twenty-seven examples given, then it is highly improbable that either of the constituents of a liquid can have present within it molecules of two or more degrees of complexity, such as one must presume to exist on the consideration of the non-integral values derived by the Ramsay and Shields' method and its numerous modifications, or Traube's or Guye's or any other method depending on the study of properties very varied in character; and the improbability is all the greater when it is remembered that Holmes's numbers are derived from measurements made at purely arbitrary temperatures at which the liquids are far from being at corresponding states.

Again, the degree of complexity deduced by the method appears to be independent of the nature of the second component of the mixture, for the value arrived at is the same; for example, when ethyl alcohol is mixed with water, or with ethyl ether, methyl iodide, or carbon disulphide, results wholly at variance from those obtained by freezing-point and boiling-point measurements, which indicate that the nature of the solvent is a powerful factor in modifying molecular liquid state (compare Auwers, *Zeit. Phys. Chem.*, 1899, xxx., 300; Meldrum and Turner, *Trans.*, 1908, xciii., 876; 1910, xcvi., 1605; Turner, *Trans.*, 1911, xcix., 880).

The third point mentioned above is equally important. Against the probability that *n*-hexane, benzene, and carbon disulphide are associated in the way Holmes believes, there is much evidence from a consideration of several properties. It would, for example, not be easy to reconcile the great complexity of $(\text{CS}_2)_{16}$, of molecular weight 1216, with a boiling-point as low as 46° . There are, however, more fundamental objections. Consider the substances ethyl ether, ethyl acetate, benzene, *n*-hexane, chloroform, and carbon disulphide, all of which Holmes considers so complex. In the state of vapour they each occupy a volume corresponding with the simplest possible molecular formula, and if, therefore, any alteration of complexity occurs, it must be presumed to take place when the vapour condenses. If, therefore, the temperature of the mixture of liquid and vapour be raised towards the critical point, either the molecular complexity of the liquid must decrease (which on Holmes's view is improbable, as shown above) or that of the vapour must increase, since liquid and vapour become identical at the critical point. Now when vapour and liquid are of different degrees of complexity, it has been found (Young, *Phil. Mag.*, 1892, [5], xxxiv., 503; Young and Thomas, *Trans.*, 1893, lxi., 1191; Young, "Stoichiometry," Long-

mans, 1908; compare Ramsay, *Proc. Roy. Soc.*, 1894, lvi., 171) that the various critical relationships are abnormal. Water, the alcohols, and acetic acid, all of which Holmes agrees are associated, are abnormal; but benzene, *n* hexane, ether, ethyl acetate, and alkyl iodides are not, and one may conclude that the complexity of the liquid and vapour undergoes little or no change. Similarly, it is possible from the value of the surface tension of a liquid at the ordinary temperature (Ramsay and Shields, *Trans.*, 1893, lxiii., 1089) or from the viscosity (Batschinski, *Zeit. Phys. Chem.*, 1911, lxxv., 665) to calculate with a fair degree of accuracy the critical temperatures of benzene, ether, ethyl iodide, ethyl acetate, and carbon disulphide, whereas with the unquestionably associated substances this is quite an impossible matter.

In conclusion, it may be pointed out that Holmes's results are deduced from solutions, and not from the pure liquid itself, in which case, despite the strength of solution used, there should be at least some measure of comparison between his results and those derived from methods based on osmotic-pressure determination. Actually, results of an opposite character are found, hydrocarbons and their halogen derivatives, ethyl acetate, carbon disulphide, &c., to which Holmes assigns a high degree of complexity, being quite unassociated by freezing-point and similar tests. It therefore follows from what has been said, that if Holmes's method is correct, temperature has no effect on the degree of complexity of a liquid; and present interpretations of critical data, as also van't Hoff's laws of solution, are untenable. If, on the other hand, they are correct, Holmes's deductions cannot be. In the author's opinion, Holmes's numbers cannot represent the molecular complexities of liquids, either actual or relative.

38. "Phytin and Phytic Acid." By GEORGE CLARKE. A detailed description of work of which a preliminary account has already appeared (*Proc.*, 1913, xxix., 27).

39. "Sulphonyl and Carbonyl Derivatives of Aniline. Resolution of Externally Compensated *p*-Toluenesulphonyl alanine into its Optically Active Components." (Preliminary Note). By CHARLES STANLEY GIBSON.

In continuation of the work of Pope and Gibson (*Trans.*, 1912, ci., 939), a comprehensive stereochemical study of derivatives of aniline and other amino-acids is being undertaken.

The method of preparation of externally-compensated *p*-toluenesulphonylalanine has been conveniently modified, and the compound has been resolved into its optically active components by the method of Pope and Gibson (*loc. cit.*).

One equivalent of *p*-toluenesulphonylalanine was treated in boiling aqueous solution with half an equivalent each of strychnine and sodium hydroxide, and after allowing the clear solution to remain, an almost theoretical quantity of the strychnine salt of *d*-*p*-toluenesulphonylalanine separated. This was re-crystallised from very dilute alcohol, and obtained in clusters of colourless needles, melting at 188–189°. The acid remaining in the mother-liquor from the separation of the strychnine salt was then isolated, and treated with the corresponding quantities of brucine and sodium hydroxide in boiling water. After some time a good quantity of the brucine salt of *l*-*p*-toluenesulphonylalanine separated. This was re-crystallised from a large quantity of boiling water, and obtained in long colourless prisms, melting at 148–149°.

d-*p*-Toluenesulphonylalanine,—



was obtained in the usual manner from the strychnine salt, and after one recrystallisation from aqueous alcohol it was found to be pure, and separated in long colourless needles, melting at 131–132°. Its rotation was determined in alcoholic solution at 25°.

0.5894, made up to 25 cc. and observed in a 2-dcm. tube, gave $\alpha_D +0.37^\circ$, $[\alpha]_D +7.71^\circ$.

In a similar way *l*-*p*-toluenesulphonylalanine was isolated

from the brucine salt, and this was obtained pure after two recrystallisations from aqueous alcohol. It appeared in well-defined colourless crystals, melting at 131–132°. The melting-point of the racemic compound is 138–139° (*loc. cit.*). The rotation of the *l*-*p*-compound was determined under the same conditions as the above:—

0.5472 gave $\alpha_D -0.35^\circ$, $[\alpha]_D -7.62^\circ$.

The completion of this and other investigations is being delayed so that the final observations may be made under better and more accurate conditions.

40. "The 'Azeotropic' Mixtures of Ethyl Acetate and Water." By ROBERT TABOR LATTEY.

Although its derivation signifies "unchanged by boiling," Wade defined an azeotropic mixture as one of maximum (or minimum) boiling-point. The mixtures of ethyl acetate and water described by Merriman (*Trans.*, 1913, ciii., 1798) do not strictly fall under this definition. The points representing their composition and pressure on a P/x diagram are three—two for liquid phases and one for vapour phase. None of these is a maximum point; that representing the vapour phase is the intersection of two curves. This was pointed out in the case of triethylamine and water, where similar conditions prevail (*Trans.*, 1907, xci., 1959). It is not possible to construct the complete P/v curve (y = molecular fraction of water in vapour) from Merriman's data, but its correct form at 37.55° is shown in the accompanying figure. The right-hand branch cannot have the form assigned to it by Merriman, since $p_2 = yP$ by definition and p_2 is very nearly constant for the water-vapour in contact with its solutions in ethyl acetate at each of the temperatures investigated.

For a true azeotrope, $\frac{dP}{dy} = 0$. In the case of ethyl acetate and water, $\frac{dP}{dy}$ has two values for the vapour in contact with mutually saturated solutions. At 37.55° these are given by the two values of—

$$\frac{y-x}{y(1-y)} P,$$

namely,

$$\frac{0.231-0.169}{0.231 \times 0.769} P \text{ and } \frac{0.231-0.986}{0.231+0.769} P = +70 \text{ and } -850,$$

using Merriman's data.

There is a hypothetical azeotrope in this case having the composition $x=y=0.25$ (approximately). This cannot be realised, since the liquid separates into two layers. The horizontal line in the figure indicates the composition at A and B of the saturated liquid phases, and at C of Merriman's so called "azeotrope." Liquid and vapour cannot co-exist under conditions indicated by points above the line ACB. For, suppose a solution were prepared having $x >$ that corresponding with the point A, for example, $x=0.18$, the vapour corresponding with this liquid would have a composition between $y=0.23$ and $y=0.25$, and exert a pressure of about 205 mm. Such a vapour is saturated at about 194 mm., and would, therefore, undergo partial condensation. Distillation would therefore go on until two liquids, A and B, had formed.

The second (hypothetical) maximum at about $x=0.85$ does not indicate an azeotrope. It is true that—

$$\frac{dP}{dy}, \frac{dp_1}{dx}, \text{ and } \frac{dp_2}{dx}$$

are all zero. It is, however, not necessary that $\frac{dP}{dx}$ shall also be zero, and hence—

$$y = x \cdot \frac{dP}{dy}$$

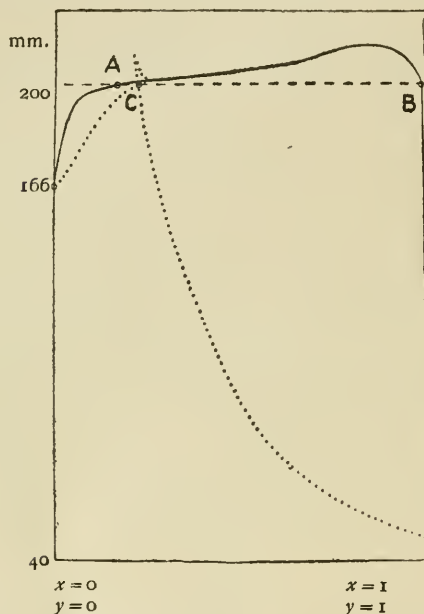
does not change signs here, since both dP and dy change signs. If the following forms of the equation deduced by Duhem, Margules, and Lehfelt are examined:—

$$\frac{dP}{dy} = \frac{y - xP}{y(1-y)} \text{ and } \frac{dP_2}{dy} = \frac{1-x}{1-y} P \text{ and } \frac{dP_1}{dy} = -\frac{x}{y} P,$$

it is seen that (i.) if $y = x$ the total and partial pressure curves all have maxima or minima, that is, an azeotrope is formed; (ii.) it does not follow that because—

$$\frac{dP}{dx} = 0, \text{ either } \frac{dP}{dy} = 0 \text{ or } y = x.$$

On page 1799 (*loc. cit.*) Marshall's equation has been misinterpreted: x represents the composition of the liquid. As Merriman points out, x has two values (corresponding



VAPOUR PRESSURES OF ETHYL ACETATE AND WATER
AT 37.5°.

with the two layers) in the case considered, and neither of these is the same as y for the vapour. Marshall's equation is another way of writing $y = x$ when $\frac{dP}{dy} = 0$, and since, as has been shown above, this condition is not fulfilled, the equation is not applicable. The calculation carried out by Merriman is simply an application of Dalton's law of partial pressures.

(We are indebted to the Chemical Society for permission to reproduce the accompanying woodcut.)

41. "Direct Combination of Nitrous Acid with Primary, Secondary, and Tertiary Amines." By PANCHANAN NEOGI.

Having isolated the nitrites of the primary, secondary, and tertiary amines from mixtures of their hydrochlorides and alkali nitrites (Neogi, *Proc.*, 1911, xxvii., 242; *Trans.*, 1912, ci., 1610; *CHEM. NEWS*, 1913, cviii., 53, 62), the author advanced the theory that an amine nitrate is formed as an intermediate compound in the interaction of nitrous acid and the amines (excepting purely aromatic amines). In continuation of the same subject, the direct action of free nitrous acid and free amine at a low temperature has been studied. It has been found that with suitable precautions pure amine nitrites are obtained by the combination of ice-cold solutions of free nitrous acid with the amines. In this way, ammonium, methylammonium, diethylammonium, trimethylammonium, benzylammonium, and piperidinium nitrites have been obtained.

42. "The Mechanism of Nitrification." (Preliminary Note). By ERNEST MOORE MUMFORD.

Investigation was directed to the bacterial oxidation of

aqueous solutions of ammonium salts on suitably inoculated experimental filters with a view to identify intermediate products of oxidation and determine the internal mechanism of the change.

The filters were inoculated from actively nitrifying sewage filters, the organism being checked by the customary methods.

As a result of the work, it has been found that the oxidation proceeds in a series of stages compatible with the hypothesis that bacterial oxidation is attained by successive hydroxylation of hydrogen atoms, and subsequent elimination of water.

Intermediate compounds were identified in hydroxylamine salts and salts of hyponitrous and nitrous acids, and it was found that the loss of nitrogen, which invariably takes place to a certain extent on such filters, is due in part to complex interactions between these various intermediate compounds; and, as the relative concentration of these compounds is determined by the degree of aeration of the filter, this hypothesis is in correlation with the observed difference in the loss of nitrogen between a percolating filter and a contact bed.

The hydroxylamine was identified by the sodium nitroprusside reaction, and estimated by titration with iodine solution in presence of sodium hydrogen carbonate, and the hyponitrous acid was detected by the formation of the insoluble silver salt; the nitrous and nitric acids were determined by the customary methods employed in water analysis.

43. "α- and β-Trimethyl Cobalticyanide." By ERNALD GEORGE JUSTINIAN HARTLEY.

Silver cobalticyanide and methyl iodide react at a temperature of about 45° to form silver iodide and two isomeric trimethyl cobalticyanides, together with some decomposition products. The two isomerides differ both in physical and chemical properties. One of them, which it is proposed to call the α-compound, is less soluble than its isomeride in water and the lower alcohols. It crystallises from hot water in very fine hair-like fibres somewhat resembling glass-wool.

It forms double salts with silver cobalticyanide and with silver nitrate.

The β-variety crystallises in minute needles from any of the above solvents. It also forms double salts with silver cobalticyanide and silver nitrate respectively, but of different composition from the corresponding α-compounds.

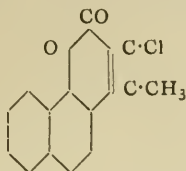
44. "The Preparation of Dithiobenzoic Acid." By GERALD NOEL WHITE.

The following simple method of preparing dithiobenzoic acid, $C_6H_5 \cdot CS_2H$, directly from benzaldehyde in one operation has been found to give satisfactory results.

A solution of 18 grms. of benzaldehyde in 300 cc. of alcohol and 150 cc. of ammonia (D 0.880) is mixed with powdered sulphur (10 grms.), and the mixture then saturated with hydrogen sulphide, first at the ordinary temperature, and finally, with frequent shaking, on the water-bath. The treatment with hydrogen sulphide is continued until all the sulphur has dissolved, and on dilution of a sample with water, no appreciable precipitate of benzaldehyde is obtained. The deep red liquid, after being diluted and shaken with benzene to remove a small quantity of unchanged aldehyde, is acidified with hydrochloric acid. The precipitate is collected and washed with ether, which is also employed to extract the dithiobenzoic acid from the acidified liquid. The substance is readily obtained as a purple oil by treating the concentrated ethereal solution with methyl alcohol.

45. "Condensation of Ethyl α-Chloroacetoacetate with Phenols." By BIKAN BIHARI DEY.

On condensing α-naphthol with ethyl α-chloroacetoacetate under suitable conditions in the presence of concentrated sulphuric acid at 0°, 3-chloro-4-methyl-1 : 2-α-naphthayrone, —



is obtained in a 70—75 per cent yield. It crystallises from glacial acetic acid in clusters of hard colourless needles, melting at 227°. On boiling it for several hours with excess of 30 per cent alcoholic potassium hydroxide, crystals of the sodium salt of α -naphthacoumarilic acid slowly separate out, which, on acidification, is converted into the free 2-methyl α -naphthafuran-1-carboxylic acid, prepared by Hantzsch and Pfeiffer (*Ber.*, 1886, xix., 1303). It melts at 248°, about 6° higher than that given by Hantzsch and Pfeiffer.

m-Cresol condenses with ethyl chloroacetate to give an almost quantitative yield of 3-chloro-4:7-dimethylcoumarin, $C_{11}H_9O_2Cl$, crystallising from alcohol in long needles melting at 135°. On boiling with alcoholic potassium hydroxide, it is converted into 2:5-dimethylcoumarilic acid, melting at 218°; Fries and Fickewirth (*Annalen*, 1908, cccxii., 51), who obtained it from the product of bromination of 4:7-dimethylcoumarin, gave 212° as the melting-point.

p-Cresol under similar conditions forms 3-chloro-4:6-dimethylcoumarin, crystallising from acetic acid in colourless needles melting at 160°; boiling alcoholic potassium hydroxide converts it into 2:4-dimethylcoumarilic acid prepared by Hantzsch and Lang (*Ber.*, 1886, xix., 1299).

o-4-Xylenol under the same treatment gives an 80 per cent yield of 3-chloro-4:6:7-trimethylcoumarin, $C_{11}H_{11}O_2Cl$, crystallising from alcohol in needles melting at 170°. It is converted by alcoholic potassium hydroxide into 2:4:5-trimethylcoumarilic acid, $C_{12}H_{12}O_3$, crystallising from ethyl acetate in colourless needles melting at 249°. On distilling the acid with excess of dry lime, the corresponding trimethylcoumarone, $C_{11}H_{12}O$, passes over as an oil, which solidifies on cooling in ice; it crystallises from acetone in snowy flakes melting at 39—40°.

Phloroglucinol gives a good yield of 3-chloro-5:7-dihydroxy-4-methylcoumarin, $C_{10}H_7O_4Cl$, crystallising in yellow needles melting at 308°. The dimethyl ether, $C_{12}H_{11}O_4Cl$, forms aggregates of short needles melting at 170°. The diacetyl derivative, $C_{14}H_{11}O_6Cl$, forms needles melting at 154°, and the dibenzoyl derivative, $C_{24}H_{15}O_6Cl$, crystallises in rhombic plates melting at 186°.

Hydroxyquinol gives a rather poor yield of 3-chloro-6:7-dihydroxy-4-methylcoumarin, $C_{10}H_7O_4Cl$, crystallising in nearly colourless needles, and melting at 259—260°. The diacetyl ($C_{14}H_{11}O_6Cl$) and the dibenzoyl ($C_{24}H_{15}O_6Cl$) derivatives melt at 172° and 192° respectively.

46. "The Action of Phosphoric Oxide on Dibenzylmalonic Acid." By HUBERT CYRIL CUTTS.

As 1-hydrindone may be prepared by the intramolecular condensation of phenylpropionyl chloride (Kipping, *Trans.*, 1894, lxx., 480), it seemed probable that dibenzylmalonic acid might be converted into a compound of the constitution $C_6H_4 \begin{smallmatrix} <CH_2> \\ <CO> \end{smallmatrix} C \begin{smallmatrix} <CH_2> \\ <CO> \end{smallmatrix} C_6H_4$. Attempts to bring about this change by means of phosphoric oxide resulted in the isolation of two products melting at 145° and 78° respectively. The investigation of these compounds and of their derivatives was just on the point of completion (last July) when further experiments were rendered superfluous by the publication of a paper by Leuchs, Wutke, and Gieseler (*Ber.*, 1913, xlv., 2200). The results of these investigators, who, however, employed thionyl chloride, and the facts established by the author, showed that the compound melting at 145° was the *O*-dibenzylacetyl derivative of 1-hydroxy-2-benzylidene, and the compound melting at 78°, dibenzylacetic anhydride.

47. "The Relation between the Absorption Spectra of Acids and their Salts." Part II. By ROBERT WRIGHT.

The examination of a number of acids and salts, with reference to their light absorbing power, seems to point to the following conclusions:—(1) The absorption spectra of strong acids are identical with those of their sodium salts; (2) moderately strong acids, such as acetic, &c., are more absorbent than their sodium salts, but the difference between the spectrum of an acid and its salt diminishes with the weaker homologues; (3) very feeble acids, such as hydrogen sulphide or arsenious acid, are less absorbent than their salts. The generalisations given do not, of course, apply to those cases where the acid and salt are of different structure.

NOTICES OF BOOKS.

The Chemistry of the Radio-elements. Part II. *The Radio-elements and the Periodic Law.* By FREDERICK SODDY F.R.S. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

THIS very important and interesting monograph deals with recent advances in our knowledge of the chemistry of the radio-elements, and their bearing upon theories of chemistry in general, and in particular upon the Periodic Law. It has been conclusively established that the method of treating the radio-elements as the analogues of known elements, with which they are chemically identical, is general, and moreover it has been proved to be generally true that an α -ray change means a shifting of the element two places to the left in the Periodic Table, while a β -ray change means the shifting of the element one place to the right. Thus a definite relation has been proved to exist between the sequence of radio-active changes and the chemical character of the products. The author has suggested the word "isotopes" "isotopic" for all elements which occupy the same place in the Periodic Table and are chemically non-separable, and the monograph contains a diagram showing the three disintegration series arranged across the Periodic Table, and the positions of the isotopic elements. The author considers that it has been abundantly proved that chemical properties alone, in the absence of any other evidence, are very insufficient criteria on which to judge the homogeneity of any material, and he regards the atomic weight of an element as a mean rather than a natural constant. The discussion of the nature of the end-products of the three series and their relation to ordinary lead is exceedingly interesting, and it is shown that chemical science has now actually discovered the way to approach the solution of the problem of the alchemist, for either the expulsion of one α -particle from thallium, or one α - and one β -particle from mercury, would give a product which would be isotopic with gold. The monograph is a highly important contribution to our knowledge of the chemistry of the radio-elements, and should be carefully studied by all who are interested in modern researches upon the structure of matter.

The Nature of Enzyme Action. By W. M. BAYLISS, M.A., D.Sc., F.R.S. Third Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

THE general properties or enzymes and methods of preparing and investigating them are exhaustively discussed in this book, the third edition of which has undergone extensive revision and amplification. Some chapters, for instance those on Reversibility and on the Combination between Enzyme and Substrate, and also the section on Anti-enzymes, have been almost entirely re-written, and recent discoveries in these regions are fully described. Many important additions have been made to the bibliography which is a valuable feature of the monograph.

The Observer's Handbook. Published by the Authority of the Meteorological Committee. Annual Edition. 1913. This handbook will be found quite invaluable by those who are interested in taking meteorological observations. It contains directions for the use of all the common types of instruments, and also discusses non-instrumental observations, giving illustrations of cloud forms and tables of the Beaufort notation and international symbols. All the tables necessary for the conversion from British to Continental units and *vice versa* are included, with specimens of returns from normal climatological stations.

Die Industrie der Cyanverbindungen. ("The Industry of the Cyanogen Compounds"). By Dr. HIPPOLYT KÖHLER. Braunschweig: Friedr. Vieweg und Sohn, 1914. (Mk. 8).

THE demand for cyanogen derivatives has risen enormously in recent years, and the working up of processes for preparing them on a large scale has engaged the attention of many scientific men. This monograph gives a clear summary of the development of the industry and its present position. It is divided into three parts. The first deals with the scientific aspects of the subject, and describes in outline the chemistry of cyanogen and its derivatives. In the second part the processes employed technically for the preparation of cyanogen compounds are discussed, including methods based upon the utilisation of animal products and the products of distillation and methods in which the atmosphere is used as the source of nitrogen. The economical aspects of the different processes are considered, and statistics of cost, &c., are freely quoted. In the third section on the analysis of cyanogen compounds the methods of testing the raw material and end-products which are adapted for technical purposes are fully described.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 2, January 12, 1914.

Melting-point of Arsenic.—R. Gouban.—In order to determine the melting-point of arsenic the author introduced freshly sublimed arsenic into a quartz flask provided with a long narrow neck and filled with an inert gas. The closed end of a quartz tube, intended for the thermo-electric couple, was pushed down to the bottom of the flask. Round the upper half of the neck a lead coil was placed, and a rapid current of cold water was passed through it. The flask was then sunk, as far as half-way up the neck, into dry sand in a graphite crucible, and the whole was heated slowly in a Roessler gas-furnace. The arsenic vapours formed as soon as the heating began drove out the inert gas, and were condensed in the cooled neck, thus forming an effectual stopper. The thermometer rose steadily to 817°, which is apparently the melting-point of arsenic. The substance possesses a high vapour tension before this temperature is reached. If the heating is continued a violent explosion occurs at about 900°.

Two Compounds of Zirconium Chloride with Pyridine.—Ed. Chauvenet.—Matteus has already described a compound of zirconium chloride and pyridine of formula $ZrCl_4 \cdot 2C_5H_5N$. Zirconium chloride is very soluble in pyridine, and on slow evaporation of the solution prismatic crystals are deposited. They have an appreciable tension of dissociation at the ordinary temperature, and often partially decompose when attempts are made to isolate them. The composition of the product generally lies between $ZrCl_4 \cdot 3.5C_5H_5N$ and $ZrCl_4 \cdot 4C_5H_5N$. The determination of the heat of fixation of n molecules of

pyridine by $ZrCl_4$ (n lying between 2 and 4) shows that no compounds exist between $ZrCl_4 \cdot 2C_5H_5N$ and $ZrCl_4 \cdot 4C_5H_5N$. Water decomposes this product, setting free zirconium hydrate. The decomposition of $ZrCl_4 \cdot 4C_5H_5N$, which begins at the ordinary temperature, takes place more rapidly at 50°, or *in vacuo* at 15°. The loss of weight ceases when the composition of the substance corresponds to $ZrCl_4 \cdot 2C_5H_5N$.

Atti della Reale Accademia dei Lincei.

Vol. xxii. [ii.], No. 11, 1913.

Preparation of Potassium Fluomanganite.—I. Bellucci.—To prepare potassium fluomanganite finely powdered potassium permanganate is warmed in hydrofluoric acid containing potassium fluoride, and after allowing to cool sulphuric ether is added drop by drop. When all the permanganate has dissolved the whole is allowed to stand, when a copious yellow precipitate forms and may be separated by decantation. The fluomanganite may be purified by re-crystallisation from 40 per cent hydrofluoric acid.

MISCELLANEOUS.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 2nd inst.; Sir James Crichton Browne, Treasurer and Vice-President, in the Chair. Sir James Key Caird, Bart., Dr. Thomas W. Dewar, Prof. Frederick G. Donnan, Dr. A. Hair, Mrs. Eric Hambro, Mr. C. E. Hearson, Mr. J. Gregory Jones, Mr. J. E. Kingsbury, Captain C. Morley Knight, Dr. Vincent W. Low, Mrs. Penrose-Thackwell, and Prof. W. J. Pope were elected Members.

Compounds of Monovalent Nickel.—I. Bellucci and R. Corelli.—When nickel cyanide of formula $NiCy_4K_2$, containing divalent nickel, is reduced in alkaline aqueous solution by nascent hydrogen (using excess of potassium amalgam), a more or less intense red coloration is produced, owing to the formation of the cyanide, $NiCy_3K_2$, containing monovalent nickel. This latter is analogous to the copper salt, $CuCy_3K_2$. The red solution of $NiCy_3K_2$ is not precipitated by the addition of ammonium sulphide.—*Atti della Reale Accademia dei Lincei*, 1913, xxii., No. 10.

MEETINGS FOR THE WEEK.

TUESDAY, 10th.—Royal Institution, 3. "Modern Ships," by Prof. Sir John H. Biles, D.Sc., &c.

WEDNESDAY, 11th.—Royal Society of Arts, 8. "Bacterial Treatment of Peat, and its Application as a Fertiliser," by Prof. W. B. Bottomley.

THURSDAY, 12th.—Royal Institution, 3. "Heat and Cold," by Prof. C. F. Jenkin, M.A.

— Royal Society. "A Functional Equation employed by Sir George Stokes," by Sir James Stirling. "Mercury Green Line $\lambda = 5461$ as resolved by Glass and Quartz Lummer Plates, and on its Zeeman Components," by J. C. McLennan and A. R. McLeod. "Electrical Condition of a Gold Surface during the Absorption of Gases, and their Catalytic Combustion," by H. Hartley. "Diffusion of Electrons through a Slit," by J. H. Mackie. "Rate of Solution of Hydrogen by Palladium," by A. Holt.

FRIDAY, 13th.—Royal Institution, 9. "An Indian State," by Sir Walter R. Lawrence, Bart.

— Alchemical Society, 8.15. (At International Club, Regent Street, S.W.). "Roger Bacon," by B. R. Rowbottom.

— Physical, 8. "Time Measurements of Magnetic Disturbances and their Interpretation," by C. Chree. "Ratio of the Specific Heats of Air, Hydrogen, Carbon Dioxide, and Nitrous Oxide," by H. N. Mercer. "Asymmetric Distribution of the Secondary Electronic Radiation produced by X-Radiation," by A. J. Philpot.

SATURDAY, 14th.—Royal Institution, 3. "Recent Discoveries in Physical Science," by Prof. Sir J. J. Thomson, O.M., F.R.S.

THE CHEMICAL NEWS.

VOL. CIX., No. 2833.

MAGNETIC SUSCEPTIBILITIES OF THE ELEMENTS.

By F. H. LORING.

THE magnetic susceptibilities of the pure elements are of scientific interest, and since these are rarely given in a collected form, except in compiled tables of physical and chemical constants, it may be of some interest to study these properties by suitably arranged tables. An attempt is here made to present the data in an orderly and possibly instructive form. A brief mention of the magnetic principles involved will be given first.

The familiar expression,—

$$\mu = B/H \quad (1),$$

signifies that the permeability μ is a *ratio* derived from the number of magnetic lines of force, B , per unit cross-sectional area in the iron, for example (say, per square centimetre), divided by H , the number of magnetic lines of force that would be developed in the same unit area of air, or empty space, the magnetising force being the same in each case. That is to say, a coil carrying a given current (or, to be more precise, of given ampère turns) will produce more magnetic lines of force in the iron within it than in the air or empty space when the iron is removed, and this ratio, whatever it may happen to be, is termed the *permeability*. Of course, tests in proof of this relation have been made under *suitable conditions* which need not be detailed here.

The permeability varies with the quality, state, history, &c., of the iron, as to whether it is soft, hard, &c. The magnetising force, H , coincides with the magnetic lines producible in the air or empty space, and these descriptive terms are exchangeable, as space or air free from magnetic substance has no varying permeability or multiplying power, being taken as *unity*. In other words, the number of magnetic lines of force in free space or air numerically represents the magnetising force. (The expression "magnetic lines of force" is supposed by some to have a physical meaning, as if the magnetism actually extended in thread-like lines. On the other hand, others regard this term as too descriptive, and they say that it should only be accepted as conventional, and that no such *line* conception should be entertained. However, the picturesque term is preferable, but the possibility, or even probability, that it is merely a conventional device should be kept in mind. It is true that this conception implies *direction* and the number of lines indicate *strength*, so that the expression is quite in order).

From the following Table (I.) these variables may be noted. This table is copied from "C. G. S. System of Units," 1891, p. 148, by J. D. Everett, the figures being based upon the measurements of Ewing and Bidwell on iron, which may be taken as fairly characteristic.

In this table the term k is given, which is the *magnetic susceptibility*. Iron, cobalt, and nickel have a high susceptibility which passes through a wide range of magnitude as compared with all other elements* (see Table II.), k being particularly variable in highly magnetic (ferromagnetic) metals, such as iron. The susceptibility is also a ratio, like the permeability, being the ratio of the intensity of the *induced* magnetism (I) to the magnetising force (H); the relation may be expressed thus—

$$I/H = k \quad (2).$$

* There are some rare elements which have not been thoroughly investigated in the pure state (see below).

TABLE I.

H. Magnetising force.	I. Magnetisation.	k. Susceptibility.	B. Induction.	μ . Permeability.
0.3	3	10	41	128
1.4	32	23	413	299
2.2	117	53	1460	670
3.5	574	164	7230	2070
4.9	917	187	11540	2350
6.7	1078	161	13520	2020
10.2	1173	115	14840	1450
22.3	1249	56	15710	705
78.0	1337	17	16900	215
208.0	1452	7	18500	89
585.0	1530	2.6	19800	34
24500.0	1660	0.067	45300	1.9

The term I at first glance seems unnecessary, as it is already seen that the magnetising force (H) gives rise to so many lines per square cm. (B) in the metal or substance, according to its permeability (μ). By a somewhat artificial procedure, the induction B may, however, be divided into two components, *one* being the magnetic lines of force due to the magnetising force H , as produced in empty space or air, and the *other* due to the magnetic lines of force which are *induced* or called into existence, or influenced, so to speak, by the peculiarity of the substance acted upon by the magnetising force; whether, for example, it be *para* magnetic like iron, or *diamagnetic* like bismuth; therefore, calling the intensity of magnetisation due to, or induced through, the agency of the substance, I , and the lines of magnetic force that would be produced in air or empty space H , which becomes the magnetising force, the following equation represents the union of these two factors:—

$$B = 4\pi I + H \quad (3).$$

(This equation is truly *algebraic*, since it holds good if the signs change; see below. The 4π term, or multiplier, arises from the old conception of 4π lines emanating from a sphere of unit radius (= unit pole), and appears in these calculations of the magnetic circuit).

It is therefore apparent that if the substances exercise variable positive and negative modifying influences, the magnetic susceptibility of any particular substance may be defined by the ratio of H to I , as shown by Equation 2, and this ratio, moreover, may be positive or negative, according to the inherent nature or characteristic of the material (see Tables II. and III.).

Having established the fundamental relations, it is obvious that different formulæ may be constructed thus:—

It was shown that—

$$B = 4\pi I + H,$$

and by definition of k ,—

$$I = kH;$$

hence—

$$B = 4\pi kH + H = (4\pi k + 1)H,$$

whilst—

$$B = \mu H;$$

therefore—

$$\mu = 4\pi k + 1$$

and—

$$k = \frac{\mu - 1}{4\pi},$$

which are all well-known expressions (see Ewing, "Magnetic Induction in Iron and other Metals," 3rd Edition, 1910, pp. 12 and 18).

While the permeability of air is taken as 1, and its susceptibility as zero, when studying the permeability and susceptibility of highly magnetic substances such as iron, cobalt, &c., *air*, as a matter of fact, is very feebly magnetic, and for an absolute comparison (or correction) a vacuum may be taken, which is absolute unity in one case and absolute zero in the other. The following values by volume ($k_v \times 10^6$) may be of interest in this connection:—

TABLE II.—*Paramagnetic Elements.*

		Positive susceptibilities for unit mass, given in $10^6 \times k_m$ values; k_m being the susceptibility, which may be calculated by multiplying these values by 10^{-6} .	Corresponding values for unit volume, $10^6 \times k_v$.
Fe		+31,170,000 (a) wrought iron.	
Co		+1,842,000 (b) cast cobalt.	
Ni		+2,003,000 (c) annealed nickel rod.	
O ₂		+436 at -259° (solid)	+324 at -182°
Mn		+20 " 1000° (+11 at 18°)	
Pd		+5.8 " 18° (+2 at 1100°)	+50 to +60
Cr		+4.2 " 1100° (+3.7 at 18°)	
Ti		+3.5 " 1100° (+3.1 at 18°)	
Rh		+1.9 " 1150° (+1.1 at 18°)	+13
V		+1.8 " 1100° (+1.5 at 18°)	
Nb		+1.3 " 18°	
Pt		+1.1 " 18° (+0.7 at 1000°)	+23 to +29
Ta		+0.93 " 18° (+0.8 at 800°)	
Be		+0.79 " 15°	
Al		+0.65 " 18° (+0.5 at 1000°)	+1.7 to +1.9
Mg (cryst.)		+0.57 " 20° (+0.55 at 18°)	
Na		+0.51 " 18°	
K		+0.40 " 18—180°	
Li		+0.38 " 18—1100°	
W		+0.33 " 18—1100°	
Ir		+0.3 " 1100° (+0.15 at 18°)	+4.9
Th		+0.3 " 400° (+0.18 at 18°)	
Os		+0.04 " 18—1100°	
Mo		+0.04 " 18°	
Sn		+0.03 " 18—240°	+0.35
Si (see Table III.)		+0.01 " 16° (cryst.) (St. Meyer)	+0.001 at 16°
N ₂ (atmospheric pressure)			

Explanatory Note.—The second column gives the values ($10^6 \times k_m$) for elementary substances of the first column (not single atoms). Values marked *a*, *b*, *c* are fairly characteristic, and show the enormously greater susceptibilities of these elementary substances under conditions of practically the highest susceptibility. The bracketed values show lower values for the temperatures (°C.) specified.

TABLE III.—*Diamagnetic Elements.*

		Negative susceptibilities for unit mass, given in $10^6 \times k_m$ values; k_m being the susceptibility, which can be calculated by multiplying these values by 10^{-6} .	Corresponding values for unit volume, $10^6 \times k_v$. A = atmospheric pressure.
He			-0.002 at 0° (A)
H ₂			+0.008* at 16° (A), -0.005† at 15° (A)
Ar			-0.10 at 0° (A)
Cu	-0.09 at 18—1000°		-0.66 to -0.80
Si (cryst.)	-0.12 " 18° (Honda). (See Table II.)		
Pb	-0.12 " 18—330°		-1.4 to -0.84
Zn	-0.15 " 18 (-0.10 at 650°)		-0.70 to -1.0
Au	-0.15 " 18—1060°		-3.1
Cd	-0.17 " 18° (-0.15 at 700°)		
Hg	-0.19 " 18—250°		-2.6 at 19°
Ag	-0.22 " 1100° (-0.19 at 18°)		-1.7 at 15°
As	-0.3 " 18—200°		
Se	-0.32 " 18°		-0.50 (red selenium) (-1.3 melted)
Te	-0.32 " 18—440°		-2.1 and -1.6 (-0.6 at 18°)
I (cryst.)	-0.35 " 18°		
Br	-0.38 " 18°		-1.4 at 19°
Zr	-0.45 " 18° (-0.3 at 1150°)		
S	-0.48 " 18—300°		-0.77 to -0.9
C (diamond)	-0.49 " 18—500°		
Cl ₂	-0.59 " 16° (A)		
B	-0.8 " 1100° (-0.71 at 18°)		
P (white)	-0.88 " 18°		-1.6 at melting-point
Sb	-0.94 " 18°		-5.6 to -3.8
Bi	-1.4 " 18° (-0.04 at 273—405°)		-16 at -182° (-14 at 15°)
C (arc carbon)	-2.0 " 18° (-1.5 at 1150°)		
C (graphite)			-8 at 18°

* Quincke.

† Bernstein.

In general, the Explanatory Note below Table II. applies to this table. In both tables, where no temperatures are given, it may be assumed that no appreciable variation from laboratory temperatures occurred. The unbracketed values, as in Table II., are principally the highest ones given in the Landolt-Börnstein compilation.

H ₂ at atmos. pressure	= -0.005, at 40 atmos.	= 0.000
N ₂ " "	= +0.001, " "	= +0.04
O ₂ " "	= +0.129, " "	= +6.2
Air " "	= +0.032, " "	= +1.3

Temperature in each case except first one, 16° C. (see Table III.). Water at 20° C. = -0.75.

Referring to Table III., it will be seen that no element has been discovered which has a negative susceptibility sufficiently high to make the permeability ($4\pi k + 1$) negative. A paramagnetic substance has a permeability greater than 1, and a positive susceptibility. A diamagnetic substance has a permeability less than unity or empty space, and a negative susceptibility. No known substance is more than slightly diamagnetic, bismuth having a negative volume susceptibility of -16×10^{-6} , and a corresponding permeability only slightly below 1, namely, 0.9998.

Tables II. and III. are self-explanatory. The values, except *a*, *b*, and *c*, are taken from the "Landolt-Börnstein Physical Tables," 1912, p. 1241. While a selection in each case of practically the highest value given in the Landolt-Börnstein table is made, higher values are possible in some cases under chosen conditions of maximum susceptibility. Practically all the mass values of the weakly magnetic elements are those by Honda, the field strength being 10.5 kilogauss. The usual ferromagnetic measurements are by volume, but since the specific gravity of a substance is the weight of a unit volume of the substance compared, the susceptibilities may be converted into mass values by dividing the volume values k_v by the density of the element = k_m . The suffixes are not always used, as it is understood from the context which magnitude is intended. The volume values in the tables may not be exactly convertible into the mass values given, as the figures relate to distinct experiments often conducted by different experimenters.

Recent work by K. Ihde (*Ann. Physik.*, 1913, xli., 829-853) points to higher values for manganese and chromium than shown in Table II., especially under altered physical conditions, the former element having a susceptibility $k = 88.3 \times 10^{-6}$, the field strength being 1000 lines per square centimetre. At a lower field strength a higher value is probable. Powdered manganese subjected to a field of double this strength gave $k = 66.5 \times 10^{-6}$ (coarsest powder) to 156×10^{-6} (finest powder). Chromium in a compact or massive state with a field strength of 1000 lines per square centimetre gave $k = 39.3 \times 10^{-6}$, and in a powdered state with a field strength two times greater gave $k = 33.4$ to 65.4×10^{-6} for coarse and fine powders respectively.

(To be continued).

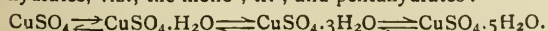
CONSTITUTION OF HYDRATES.

(PART I.).

By JAMES MACLEOD-BROWN.

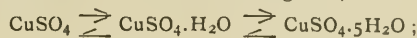
MANY papers on the behaviour and properties of salts containing water of hydration have appeared in various journals, but no explanation of the way in which the water is combined in the molecule has yet, so far as the author is aware, been generally accepted. The following theory, depending on the variability of valence, seems to be consistent with the facts:—

Cupric sulphate is usually taken to illustrate the different hydrates which a salt may form. It forms three hydrates, viz., the mono-, tri-, and pentahydrates:—



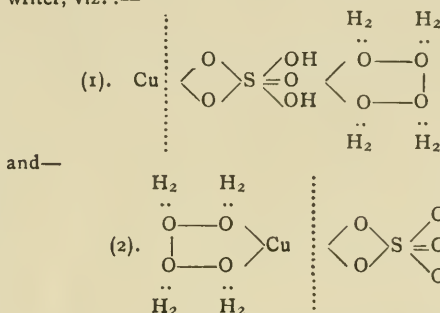
The water in the monohydrate is strikingly different from the other four molecules of water, inasmuch as it is set free at a temperature of not much below 200°. This fact tends to show that this molecule of H₂O is an entirely different function from the other four.

Of the remaining four molecules they are combined in two different ways; i.e., two of the molecules of water are combined similarly; the other two are also combined similarly, but in such a manner that they are more strongly attached than the other two. If these four molecules were all combined in the same manner the formation of CuSO₄·3H₂O would doubtless be impossible, for all the four molecules would be liberated together, thus:—



or else they could be set free individually, and a series of hydrates containing five, four, three, two, and one molecules of water respectively would be formed. As hydrates of CuSO₄ containing two or four molecules of water are unknown, the molecules must be connected as explained above.

Two constitutional formulæ have been suggested by the writer, viz.:—

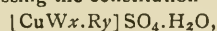


The dotted line in each case dividing anion from cation.

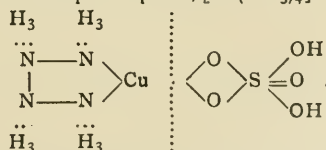
In (1) the anion is extremely complex. There are other objections to this formula which will be gone into more thoroughly in a future communication.

Formula (2) shows the anion and cation more evenly balanced. It might be objected to on the grounds that the existence of tetravalent copper is somewhat doubtful. The writer does not think this objection can hold, because the greater number of the elements are known to form compounds in which their valency varies by multiples of two. Some elements form compounds in which their valency differs by only one.

If the second formula illustrates the constitution of cupric sulphate pentahydrate we should be able to obtain compounds possessing the constitution—



where *Wx* represents number of molecules of unsubstituted OH₂ groups, *Ry* the number of groups substituted by *R*, and $x + y = 4$. Compounds of this constitution may be readily prepared in the laboratory; the best known is probably tetramminecupric sulphate, [Cu(NH₃)₄]SO₄·H₂O, or—



Part II. of this article will deal with the chemical behaviour of hydrates, viewed from the standpoint of the theory outlined above.

11, Kenil Gardens, Ealing, London, W.

Literary Intelligence.—Messrs. J. and A. Churchill have much pleasure in announcing the two following new works:—"Molecular Physics," by J. A. Crowther, M.A., Demonstrator in Physics, Cavendish Laboratory, Cambridge; with 29 illustrations. "The Synthetic Use of the Metals in Organic Chemistry," by A. J. Hale, B.Sc., Demonstrator, City and Guilds of London Institute, Technical College, Finsbury.

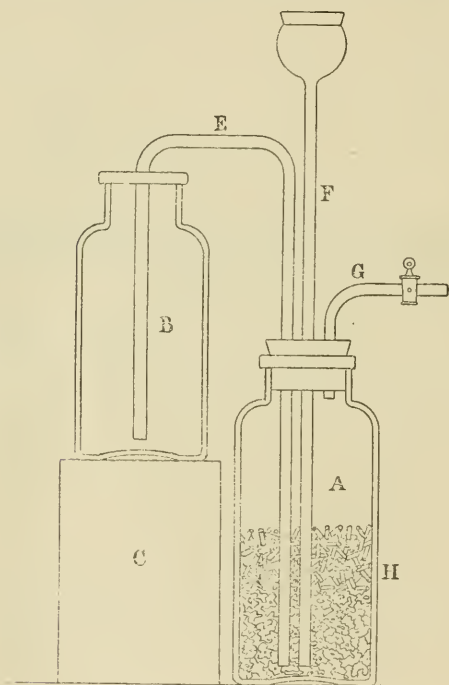
AUTOMATIC GAS GENERATOR.

By ROBERT W. CURTIS.

THE form of generator shown in the cut may be put together in a few minutes from ordinary materials at hand in any laboratory, and has a number of advantages, as will appear.

A small size may be made up as follows:—The bottle A is a 16 oz. salt mouth, B 12 oz., and the block C $4\frac{3}{4}$ in. high. The tubes E and F must fit the stopper so as to be gas tight and yet allow sliding the stopper. Size No. 4 glass tubing may be used for E in order to permit easy passage of liquid through it. The outlet G is provided with a glass stopcock, or a pinchcock could be used on the rubber connection.

In charging the apparatus the stopper is pushed up on the tubes E and F, which are held in place while pieces of broken chemically resistant material (*e.g.*, firebrick) is dropped in A to the level of H, evenly distributed by shaking. Upon this is put a layer of the material for generating the gas. The stopper is then pushed down into



place, the outlet opened, and dilute acid or other reagent, sufficient to rise above H, is added through F. When the stopcock is closed the syphon E becomes operative, and the apparatus is thereafter automatic.

A difficulty with many automatic generators is their "running down" by continuous slight action when not in use, as over night, due to a small leakage of gas. This is effectually prevented by lifting the bottle A, thus removing E from dipping in the liquid in B, and placing A where any drip from E may fall into a sink or beaker. To start up it is only necessary to replace A, and introduce enough of the liquid through F to fill E.

If the syphon is "lost" at any time it is but the matter of a moment to re-fill E similarly. If the admission thus of a little air into the gas is objectionable, a separatory funnel may be used instead of F.

The reagent in passing back and forth through E is thoroughly mixed with the spent liquor. Fresh reagent may be added at any time through F or in B, and waste

removed easily from B. The whole apparatus can be thoroughly rinsed out through F and E without disturbing any adjustments. There is no possibility of leakage of the liquid reagent. The arrangement is so simple, portable, and easily set up that a number may be constructed as needed.

If a three-necked Woulfe bottle were substituted for A the central neck could be closed by the stopper carrying the outlet G. The removal of this stopper would render easier the replenishing of the solid reagent.

The dimensions could be varied to meet different requirements; as increasing the height of C to obtain greater pressure, or the size of A to give greater reservoir capacity, or the diameter of B to increase the supply of liquid reagent without much increase of pressure.

College of the City of New York,
Feb. 12, 1914.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

THE MINERALOGICAL CONSTITUTION OF THE SHETLAND ISLES.

M. E. Gourdon, geologist of the French Antarctic Exhibition (the Charcot Mission), has studied the geological constitution of the Shetland Islands. Deception Isle affects the curious form of an almost perfect ring of land; the narrow passage by which the little inland sea communicates with the ocean measures barely 200 metres of navigable width. It is an immense crater invaded by the sea. In the island that is entirely volcanic, the glacier phenomenon is to be found side by side with the volcanic phenomenon; fumaroles of 90° are to be found even in the midst of fields of snow; layers of ice alternate with the layers of ashes. The island is formed of yellow tufas, in the midst of which crop out oozings formed by trachytes, ondesites, and labradorites. Large blocks of basalt are also to be met with.

THE MAMMOTH OF THE MUSEUM.

The mammoth found four years ago in the Liakowsky Islands in the extreme north of Siberia, and offered by the Count of Stenbock Fermor to the Paris Natural History Museum, has just been naturalised. Its state of preservation is absolutely remarkable. M. Edmond Perrier, director of the Museum, has informed the Academy of Sciences concerning the histological studies undertaken by M. Gautrelet about this proboscidean that lived several centuries ago. The muscular fibres are atrophied, but the conjunctive frame still subsists. M. Gautrelet has been able to discover, in the interior of the veins, blood that has naturally undergone great modifications, but it has kept its essential elements.

PURE METALS.

A very important progress in the preparation of refractory metals of very great pureness has just been made in the laboratories of the Institute of Applied Chemistry. Prof. Albin Haller has, in fact, presented a paper of a young and clever chemist, M. Maurice Billy, who has found a very interesting general method. This method is very simple. Up till now refractory metals were prepared by reducing their chlorides by hydrogen or by sodium. The high temperature required when hydrogen is employed, and the great difficulty of employing sodium without oxidation, have always been the cause of the impurities introduced into the metal. Thus, to prepare the most refractory metal, titanium, the method adopted was that of Petterson and Nilsen, which consists in heating to a dark red, liquid chloride of titanium in presence of sodium in a steel bomb screwed down tight. The reaction is extremely violent; the metal is almost pure, but contains traces of iron. In view of obtaining metals perfectly free from iron, silicium, and oxygen, M. Maurice Billy has made hydride

of sodium react on chloride of titanium or of vanadium at about 400°. All the inconveniences of high temperatures and violent reactions are avoided. The operations can be made in apparatus of fusible glass, and the reaction takes place in a vessel of melted sea-salt. The quantities vary according to the way the operation is performed. M. Bily has obtained as much as 50 per cent of rigorously pure metal, compared with the quantity of sodium employed. The pureness obtained is such that the titanium does not contain 1/10,000th of a mgrm. of iron. Prof. Haller remarks that it may already be considered that the reduction of metallic chlorides by hydride of sodium constitutes a general method for the preparation of pure metals, such as physico-chemistry requires to-day.

THE LONGEST TELEPHONIC CIRCUIT OF THE WORLD.

The longest European telephone lines do not exceed 1400 to 1500 kilometres. The telephonic circuit of Paris-Rome is only 1500 kilometres long and that of Paris-Vienna only 1450 kilometres. In America the length of 3200 kilometres has been attained with pupinised wires of 4 millimetres in diameter. The electric transmission can only be obtained with difficulty over greater distances. The two stumbling blocks to be avoided in telephony at a distance are the alteration of the voice caused by the distortion or diffraction of the waves of sound on the one hand and the weakening of the sound produced by the diminution of the amplitude of the waves produced on the other. A distinguished engineer, M. Drumaux, has just studied the conditions of a good transmission. In order to have an excellent result it would be necessary to space the spools of Pupin, inserted in the circuit from the twelfth or fourteenth of the wave-length; that is to say, about 10 kilometres. An American company proposes, by utilising the latest improvements of the telephonic industry, to unite New York by telephone with Los Angeles and San Francisco. The distance to be covered is about 5600 kilometres. The circuit will be constituted with copper wires of 41 millimetres in diameter, and supplied with Pupin's coils or spools, which will be placed at intervals of 14 kilometres. As on account of the difference of time between New York and San Francisco the circuit will be utilised only for a short time, the price will be fixed at a relatively high rate for the exchange of communications. These rates will reach prices unknown in Europe, and in all probability will vary from 80 to 100 francs for three minutes' conversation.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 26, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

Papers were read as follows:—

"*Diffraction of Light by Spheres of Small Relative Index.*" By Lord RAYLEIGH, O.M., F.R.S.

"*Studies of the Processes Operative in Solutions XXXI. Sulphonic Acids and Sulphuric Acid as Hydrolytic Agents: a Discussion of the Constitution of Sulphuric and other Polybasic Acids, and of the Nature of Acids. XXXII. The Influence of Sulphonates on the Hydrolytic Activity of Sulphonic Acids: a Contribution to the Discussion on the Influence of Neutral Salts.*" By Prof. H. E. ARMSTRONG, F.R.S., and Prof. F. P. WORLEY.

"*Morphological Studies of Benzene Derivatives. V. The Correlation of Crystalline Form with Molecular Structure: a Verification of the Barlow-Pope Conception of 'Valency-volume.'*" By Prof. H. E. ARMSTRONG, F.R.S., R. T. COLGATE, B.Sc., and E. H. RODD, B.Sc.

"*Magnetic Properties of Iron when Shielded from the Earth's Magnetism.*" By Prof. ERNEST WILSON.

When iron is subjected to a considerable magnetising force, a species of polarisation is produced which has the effect of reducing the permeability and increasing the dissipation of energy due to magnetic hysteresis for given values of the magnetic induction. The residual effects can be removed by careful demagnetisation or annealing. It was thought by analogy that the earth's magnetic force would also have a polarising influence upon exposed iron, and this is the subject of the present paper. An effort has been made to remove the residual effects of the earth's magnetism by placing the specimen, which is of ring form, in a magnetic shield, and carefully demagnetising it. The magnetic properties of the material were then examined in the usual manner with a ballistic galvanometer, and a comparison made with those obtained from the exposed or unshielded specimen. It has been found that the permeability of freshly demagnetised and shielded iron, corresponding to a given value of the magnetic induction, is considerably larger than in the case of the unshielded specimen. In Stallery the ratio of the permeabilities has a maximum of 1.79 when the magnetic induction is 172. The permeability rises to a maximum of 5900, and one would anticipate a considerably larger initial permeability than is generally supposed. The permeability has been examined after varying periods of rest when the specimen is in a carefully demagnetised condition, and it is shown that its values gradually decrease as the duration of rest increases. Further experiments are contemplated to discover if this diminution is due to imperfect shielding, or if the iron, when perfectly shielded, would diminish its permeability by intermolecular action. The dissipation of energy due to magnetic hysteresis is examined when the magnetic induction has values as low as 0.68. It is found that the shape of the loops suffers a marked change, becoming parallel straight lines when the smallest magnetising forces are employed. It is well known that the Steinmetz Index tends to increase as the lower forces are approached. The experiments indicate that the Index tends to again diminish both in shielded and unshielded iron.

"*Occurrence of Ozone in the Upper Atmosphere.*" By J. N. PRING, D.Sc.

This investigation was concerned with the estimation of ozone in the atmosphere at altitudes ranging up to 20 kilometres, and the distinction of this gas from other substances, such as the peroxides of hydrogen and nitrogen, which show very similar chemical reactions. A method was devised which enabled these measurement to be made under conditions which prevail in the atmosphere.

The chemical reagent used for this purpose enabled approximately quantitative results to be obtained when used in light apparatus which were attached to free balloons, and gave the following results:—

That in the Alps, at an altitude of 2100 metres, the mean concentration of ozone is about 2.5 parts by volume in 1 million of air, and at an altitude of 3600 metres about 5 parts in one million of air,

In this country the mean quantity found between ground-level and an altitude of 20 kilometres was about 2 parts by volume in 1 million. No trace of either hydrogen peroxide or nitrogen peroxide could be detected in these cases.

Measurements made in the laboratory on the action of ultra-violet light on air showed that a definite equilibrium amount of ozone is obtained, and that this value increases with fall in temperature, but decreases rapidly with fall in pressure.

The formation of hydrogen peroxide or nitrogen peroxide by ultra-violet light radiation could not be detected.

"*A Meteoric Iron from Winburg, Orange Free State.*" By W. A. D. RUDGE.

In this paper some account is given of the structure, and mechanical and magnetic properties of the Winburg

meteorite, which is stated to have fallen in 1881. It appears to be composed of large crystals of ferrite with veins and crystals of an iron nickel alloy. The total amount of nickel is not more than 3 per cent. Flakes of the alloy can readily be separated from the ferrite, owing to its insolubility in dilute acid. Very fine crystals of alloy are found enclosed in the ferrite crystals. The material will stand a stress of nearly 10 tons per square inch before yielding occurs, and in the elastic limit Young's modulus is nearly the same as that for pure irons. By submitting a piece of the metal to a pressure of 7000 lbs. dead load, "slip" bands were developed, which showed evidence of twinning having been set up. The magnetic properties are very similar to those of Swedish iron, but for moderate field strengths the susceptibility is decidedly greater, and for very strong fields somewhat less.

"Electrification produced during the Raising of a Cloud of Dust." By W. A. D. RUDGE.

During the raising of a cloud of dust a considerable amount of electrification occurs. Insulated conductors held in a stream of dust become charged to a potential of some hundreds of volts. The dust particles seem to be charged by friction amongst themselves, some with positive, others with negative, electricity. If a cloud is raised by blowing air through a wash-bottle containing finely divided material, the air accompanying the cloud becomes strongly charged, and this charge persists in the air for some time. The sign of the charge carried by the air depends upon the nature of the material. Mercury sulphide, sand, molybdc acid, and "acidic" bodies in general give negative electricity, whilst coal, flour, red-lead, alkaloids, and "basic" bodies give positive electricity. A very small amount of dust, 10^{-10} grms. per cc. will give rise to quite strong charges. The finer the material the stronger and more persistent is the charge.

"Electrical Ignition of Gaseous Mixtures." By Prof. W. M. THORNTON.

This is an experimental examination of the mechanism of ignition of gaseous mixtures by electrical sparks. It is found that there are two distinct types of curves connecting percentage of gas in air, and the least current which, when broken, causes ignition by the break-spark. In one, characteristic of continuous currents, the current required is proportional to the percentage of gas present; in the other, of alternating current type, it is a quadratic function of the percentage, having a minimum, at the mixture giving combustion, midway between CO and CO₂. In the paraffin series the minimum continuous current is the same for all the gases, but with alternating current the gases with more complex molecules require larger igniting currents. The slope of the one type and the minimum current of the other are both proportional to the number of atoms in a molecule of combustible gas, more nearly to the hydrogen atoms. It is inferred from the observations that ignition by continuous current break-sparks is largely ionic or electronic, but that that by alternating currents is more nearly a simple thermal process. The gases examined were hydrogen, carbon disulphide, benzene, alcohol, and the paraffin series up to pentane.

CHEMICAL SOCIETY.

Ordinary Meeting, February 19, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President,
in the Chair.

THE PRESIDENT referred to the loss sustained by the Society through the death of Gustavus Anthony Abrines (Gibraltar), Charles Cunningham Connor (Belfast), and Arthur Ellison Davies (Edinburgh).

Certificates were read for the first time in favour of Messrs. Arthur Baxter, B.Sc., 360, York Road, Camden Road, N.; Albert Coulthard, B.Sc., Ph.D., 9, Portland

Avenue, Stamford Hill, N.; Robinson Percy Foulds, M.Sc., Stanley Villa, Colne; Arthur Bertram Hobson, M.Sc., 13, Westy Lane, Latchford, Warrington; James Riddick Partington, B.Sc., The University, Manchester; Walter Ryley Pratt, B.Sc., 17, Bloomsbury Square, W.C.; Walter William Reeve, B.Sc., 4, Gowlett Road, East Dulwich, S.E.; Herbert Corner Reynard, B.Sc., West Ewell, Epsom.

Certificates have been authorised by the Council for presentation to ballot under By-law 1. (3) in favour of Messrs. Clifford Girdlestone Gill, Cawnpore Sugar Works, Ltd., Cawnpore, India; Yusuf Ismail Mulla, Alembic Laboratory, Club Road, Mandalay Shore, Burma.

The PRESIDENT announced that the following changes in the Offices and Council were proposed by the Council:—

Vice-Presidents to Retire—Dr. G. T. Beilby and Prof. W. Jackson Pope.

Ordinary Members of Council to Retire—Sir Boverton Redwood, Bart., Mr. W. R. Bousfield, Prof. H. Marshall (deceased), Prof. F. G. Donnan.

As President—Prof. W. H. Perkin.

As Vice-Presidents who have filled the Office of President—Prof. H. E. Armstrong, Prof. A. Crum Brown, Sir William Crookes, Sir James Dewar, Prof. H. B. Dixon, Prof. Percy F. Frankland, Dr. A. G. Vernon Harcourt, Prof. R. Meldola, Dr. H. Müller, Prof. W. Odling, Sir William Ramsay, Prof. J. Emerson Reynolds, the Right Hon. Sir Henry E. Roscoe, Sir Edward Thorpe, and Sir William A. Tilden.

As Treasurer—Dr. Alexander Scott.

As Hon. Secretaries—Dr. Samuel Smiles and Prof. J. C. Philip.

As Foreign Secretary—Prof. Arthur W. Crossley.

As Vice-Presidents—Prof. H. Brereton Baker, Prof. P. P. Bedson, Dr. Horace T. Brown, Mr. C. T. Heycock, Prof. E. J. Mills, and Prof. G. T. Morgan.

As New Ordinary Members of Council—The Earl of Berkeley, Dr. R. H. A. Plimmer, Dr. G. Senter, Prof. J. M. Thomson.

Dr. Samuel Rideal, Prof. J. J. Dobbie, and Sir Alexander Pedler were elected Auditors to audit the Society's Accounts.

Messrs. G. Fowles and H. Rogerson were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared duly elected:—Ethelbert William Blair, B.Sc.; Albert Frederick Calvert; Sydney George Clifford; Lionel Cohen; Behari Lal Dás; Sydney Edward Davenport; Thomas Alexander Davidson; Thomas Eynon Davies, B.Sc.; Richard Charles Denington; Charles George Fernie, B.Sc.; George Ingle Finch; Reginald Furness, M.Sc.; John Garth; Ivan Richard Gibbs, B.A.; James Stanley Hale; Theophilus Harper; Eric Russell Harrap; Oswald Ryle Horwood, M.A., M.R.C.S., L.R.C.P.; Manappadam Ramaswami, Viswanatha Iyer; Dan Ivor James, M.A., B.Sc.; Gopal Balkrishn Kolhatker, M.A.; Alfred John Leigh, B.Sc.; Frederic William Leighton; Alex. Williamson McLaren; Archibald Macpherson; Fredk. Arthur Makin; Thomas Morris; Raymond William Nichols; William Julian Oldum, B.A.; Rowland Ernest Oldroyd; Frederick Alfred Pickworth; William Henry Pick, B.Sc.; Conley Hunter Riley; William Pawson Robson, B.A., Ph.D.; Chandra Bhusan Roy, M.A.; Joseph de Carle Smith (junior), B.Sc.; Charles Alfred Stamp; Horace Gilbert Stone, B.Sc.; Harold Edwin Temple; Eustace Ebenezer Turner, B.Sc.; Robert James Wright, M.A.

Of the following papers those marked * were read:—

*48. *"The Production of High Vacua by Means of Finely Divided Copper."* By THOMAS RALPH MERTON.

It has been found that the vapour pressures of gases absorbed by finely divided copper are so low that the absorption of gases by this substance may be used for the production of high vacua.

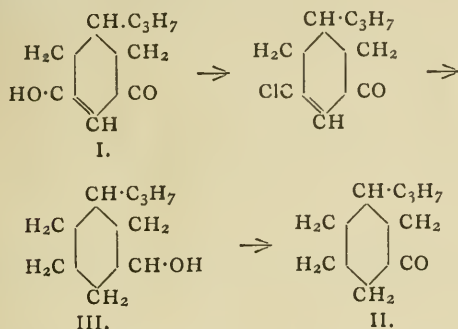
DISCUSSION.

Prof. H. B. BAKER was able to confirm Mr. Merton's results, as, in some work he had done with Prof. Strutt, a tube of copper gauze which had been left with a pressure of 1—2 mm. of nitrogen over night was found next morning to resist the passage of a very powerful electric discharge. He thought that the method would be of great importance in dealing with small traces of gases.

Dr. LOWRY suggested that the power of absorbing gases was perhaps a function of the amorphous, as contrasted with the crystalline, form of copper. This was in agreement with the fact that this power was lost on heating to 250°, a temperature that was practically identical with the annealing-temperature of hard-drawn copper wire; further, that repeated heating at lower temperatures produces the same effect.

*49. "Hydroaromatic Ketones. Part III. 1-isoPropyl cyclohexan-3-one." By ARTHUR WILLIAM CROSSLEY and WALTER RYLEY PRATT.

1-isoPropylcyclohexan-3-one (II.) has been prepared from 1-isopropylidihydroresorcin (I.) by a series of reactions indicated by the following formulæ:—



It boils at 208°, gives a semicarbazone melting at 187°, and a liquid oxime, the benzoyl derivative of which melts at 91—92°.

1-isoPropylcyclohexan-3-ol (III.) is a viscid liquid, boiling at 114°/28 mm., and possessing a characteristic pungent odour. The o-nitrobenzoyl derivative crystallises in small white prisms, melting at 47—48°. Both the alcohol and the ketone give β-isopropyladipic acid on oxidation with potassium permanganate.

It is intended to make the ketone the starting-point in the synthesis of certain meta-terpene derivatives, as it has been found possible by varying the original conditions (*Trans.*, 1902, lxxi., 676) to improve the yield of isopropylidihydroresorcin so that it may now be obtained in about 70 per cent of the theoretical amount.

*50. "The Spitting of Silver." By HERBERT BRERETON BAKER.

The amount of oxygen absorbed by melted silver is so large that it seems difficult to explain on the hypothesis of a mere solution of such a gas in such a liquid. It seemed conceivable that there might be formed an oxide of silver which was stable at high temperatures, but decomposed on allowing the temperature to fall; a case analogous to the well-known behaviour of silicon trichloride. An attempt has been made to apply a test for the presence in the molten metal of an oxide of silver. It is found that if silver oxide is dropped into melted boron trioxide silver borate is formed, although the temperature is much above the decomposition point of the silver oxide. Accordingly, some highly purified silver was melted in a stream of oxygen, a part only of the surface of the metal being covered with boron trioxide. This procedure was rendered easy by the convexity of the surface of the liquid metal, a ring of the trioxide surrounding the exposed surface. In these circumstances silver borate is formed in large quantity. If, however, the metal is covered entirely, even by

a thin film of the trioxide, no silver borate is produced. It cannot be claimed that an absolute proof of the existence of an oxide of silver has been obtained, because there is the possibility of the reaction of three substances together, no two of which will otherwise unite. It seemed worth while, however, to put the experiments on record.

*51. "The Rate of Transformation of Ammonium Cyanate in Absolute Alcohol." By JOHN DAVID McBEATH ROSS.

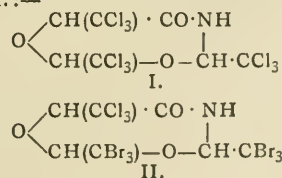
The experiments of Walker and Kay (*Trans.*, 1897, lxxi., 489) on the velocity of the transformation of ammonium cyanate into carbamide in aqueous alcohol have been extended to solutions containing more than 90 per cent of alcohol. On the assumption that the action primarily takes place between the ammonium ions and the cyanate ions, it is found that the acceleration previously observed continues up to alcohol of 99.94 per cent by volume, the increase in the speed of the transformation being most noticeable in solutions containing a large percentage of alcohol. The same conclusions hold good when the action is considered to be primarily due to the non ionised ammonium cyanate, although in this case the change in the velocity-coefficient is smaller than on the other assumption.

DISCUSSION.

Dr. SENTER referred to the contention of E. E. Walker (*Proc. Roy. Soc.*, 1912, A, lxxxvii., 539) that in determining the influence of alcohol on the rate of decomposition of carbamide in aqueous solution, the solutions should not be made up to a definite volume, but the ratio of carbamide to water should be kept constant and varying proportions of alcohol added. Apart from the objections urged by the author of the present paper, the latter method of making up solutions was open to criticism on kinetic grounds. Comparing two solutions in which the ratio carbamide : water was the same, but one of which contained alcohol in addition, the total volume of the latter was considerably greater, and therefore the number of collisions between the reacting molecules or ions, and consequently the rate of reaction differed in the two cases on spacial grounds, apart altogether from other effects. For this reason the usual method of making up to a constant volume, although not free from objection, would appear to afford a much truer representation of the effect of alcohol on the reaction than the method advocated by E. E. Walker.

52. "Condensations of Cyanohydrins. Part II. The Condensation of Chloralcyanohydrin with Chloral Hydrate and with Bromal Hydrate." By HORACE LESLIE CROWTHER, HAMILTON McCOMBIE, and THOMAS HAROLD READE.

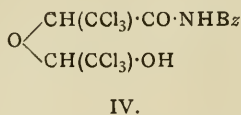
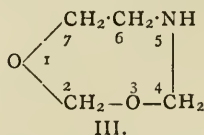
The compound described by Wallach (*Annalen*, 1874, clxxiii., 297) and Cech (*Ber.*, 1876, ix., 1020) as being formed by the action of potassium cyanide on excess of chloral hydrate has been shown by the authors to have the constitution (I.). In this reaction it is produced by the condensation of normal chloralcyanohydrin (which is first formed) with 2 molecules of chloral hydrate. This condensation has been shown to take place in the presence of potassium hydroxide. Further, using the same condensing medium, the authors have been able to condense chloralcyanohydrin with bromal hydrate with the production of compound II.:—



It has been decided to call the parent seven-membered ring (III.) 1 : 3 : 5-dioxazseptan, so that (I.) is called 6-keto-2 : 4 : 6-tri(trichloromethyl)-1 : 3 : 5-dioxazseptan.

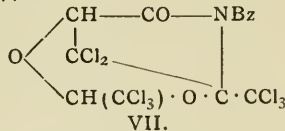
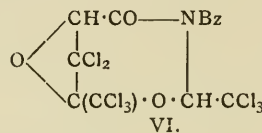
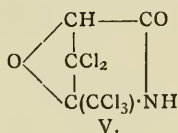
The dioxazseptan derivatives give rise to monoacyl derivatives, in which the acyl group is attached to the nitrogen atom. The benzoyl derivatives when treated

with hydrochloric acid, in glacial acetic acid, are decomposed, one chloral (or bromal) residue is eliminated from the molecule, and there results, in the case of the benzoyl derivative of (I), β -trichloro- α -(3'-trichloro- α' -hydroxy-ethoxy)-propiobenzamide (IV).—



This compound, on treatment with sodium carbonate, or hydroxide, yields 4:4-dichloro-3:5-oxido-5-trichloromethyl-2-pyrrolidone (V.), a compound which is readily soluble in alkalis, but is precipitated unchanged on the addition of acids. An analogous compound can be prepared from the benzoyl derivative of II.

Another interesting change which is undergone by the benzoyl derivatives is brought about by the action of dilute potassium hydroxide. In this case 1 molecule of hydrogen chloride is eliminated, and the resulting compound has the constitution VI. or VII.:



53. "The System: Ethyl Ether—Water—Potassium Iodide—Mercuric Iodide. Part II. Solutions Saturated with Respect to Solid Phases in the Four-component System." By ALFRED CHARLES DUNNINGHAM.

The equilibria are represented by means of a tetrahedron, of which a diagrammatic projection was shown. Saturation surfaces exist for the solid phases: potassium iodide, potassium mercuri-iodide, potassium mercuri-iodide hydrate ($\text{KHgI}_3 \cdot \text{H}_2\text{O}$), and mercuric iodide. The surfaces are divided by binodal curves into homogeneous and heterogeneous areas, on which liquid mixtures, in equilibrium with the solid phase, exist as one or two layers respectively.

In the case of potassium iodide and potassium mercuri-iodide, the homogeneous portions of the saturation surfaces are entirely separated by a heterogeneous area. This corresponds with the fact that in contact with either of these phases, water and ether are only miscible to a very limited extent.

In the case of potassium mercuri-iodide hydrate and mercuric iodide, the saturation surfaces are divided into homogeneous and heterogeneous portions by critical curves. The homogeneous portions thus formed extend almost across the tetrahedron, corresponding with the fact that in contact with these phases water and ether can become miscible in almost all proportions.

54. "The Connection between the Dielectric Constant and the Solvent Power of a Liquid." By WILLIAM ERNEST STEPHEN TURNER and CRELYN COLGRAVE BISSETT.

In a series of investigations on the factors affecting the solubility of electrolytes, Walden (*Zeit. Phys. Chem.*, 1906, lv., 683) drew the conclusion that a parallelism exists between dielectric constant and solvent power, and later (*Zeit. Phys. Chem.*, 1908, lxi., 633) formulated an expression, $\epsilon/\mu = \text{constant}$, applicable to tetraethylammonium and tetrapropylammonium iodides dissolved in a number of solvents, ϵ representing the dielectric constant of the solvent, and μ the molecular percentage solubility of the solute.

It was now shown that this expression is not generally valid, and does not apply to the solubility data of Peddle and Turner (*Trans.*, 1913, ciii., 1202) or of Turner and Bissett (*Trans.*, 1913, ciii., 1904), and on investigation with additional solvents it does not apply, as Walden considered it did, to tetrapropylammonium iodide. An attempt to find another equation was unsuccessful, and it was pointed out that the order of solvent action is in many cases not the order in which the dielectric constants run. Solvent action depends both on the nature of the solute and on that of the solvent.

It was further shown that the solvent action of a number of liquids on *p*-nitrobenzyl chloride and trimethylamine, as measured by Halban (*Zeit. Phys. Chem.*, 1913, lxxxiv., 129), and on carbon dioxide and nitrogen (Just, *Zeit. Phys. Chem.*, 1901, xxxvii., 342), is not connected with their dielectric constants.

55. "The Viscosities of some Binary Liquid Mixtures Containing Formamide." By ERNEST WYNDHAM MERRY and WILLIAM ERNEST STEPHEN TURNER.

The viscosities of mixtures of formamide with water, methyl and ethyl alcohols, formic, acetic, propionic, and *n*-butyric acids have been determined at temperatures of 25° and 40°. From the results of the investigation it was concluded that:—(1) Formamide and the lower alcohols give viscosity curves differing little from the straight line, but as the series is ascended, the calculated and observed viscosities differ by a value which is at first negative and later becomes positive, until, with *isoamyl* alcohol, a curve is obtained which contains a maximum point. The experimental values in the last case were drawn from those of Drucker and Kassell (*Zeit. Phys. Chem.*, 1911, lxxvii., 367).

2. Formamide and the aliphatic acids give viscosity curves resembling in general character those obtained with aqueous solutions of these acids, there being no maximum point with formic acid, although the calculated values are less than the observed. In the other cases, maximum points were obtained on the curve.

3. Maximum points on viscosity curves are not always due to the formation of compounds, and that, in consequence, viscosity measurements do not form a trustworthy method of testing for the formation of compounds in solution.

4. With a series of associated similarly constituted liquids, each mixed with a common associated liquid, the observed viscosity departs more and more from the calculated value as the molecular weight increases in the series.

56. "The Conversion of d-Glucosamine into d-Mannose." By JAMES COLQUHOUN IRVINE and ALEXANDER HYND.

A detailed account of an investigation, the results of which have already been communicated in the form of a preliminary note (*Proc.*, 1913, xxix., 306).

57. "The Catalytic Activity of Acids in Ethyl-alcoholic Solutions." By HARRY MEDFORTH DAWSON and FRANK POWIS.

Measurements of the rate of isomeric change of acetone under the catalytic influence of acids have been made in ethyl-alcoholic solution. From similar experiments in aqueous solution (*Trans.*, 1913, ciii., 2135) it was previously found that the catalytic effect of the acid can be represented as the sum of effects produced by the ionised and non-ionised acids. The data for alcoholic solutions also indicate that the "hydrogen ion" is not the only active component, but that the non-ionised acid is also possessed of considerable catalytic power.

It was shown that the observations in aqueous solution afford no information as to the real nature of the ionic catalyst, but that some light is thrown on this question by a comparison of the phenomena of catalysis in water and alcohol. If a comparison is made between aqueous and alcoholic solutions of acids according to their electrical conductivity, in which the acids are ionised to about the same extent, it is found that the speed of the catalysed reaction in alcohol is many hundred times greater than in

water. This is explained by the assumption that the active ionic catalyst is the free hydrogen ion which is present in very small concentration in aqueous solutions of acids, but in relatively much greater concentration in alcoholic solution. The retarding influence of small quantities of water on the velocity of this and other reactions in alcoholic solution is in agreement with this hypothesis.

58. "*Heats of Evaporation; Association in Liquids and Mixtures of Liquids.*" By JAMES RIDDICK PARTINGTON.

The equation of Bakker for the latent heat of evaporation of a liquid, which is deduced from the characteristic equation of van der Waals, gives results in poor agreement with experiment. It was shown that the characteristic equation of D. Berthelot leads to an equation giving results in much closer agreement with the experimental numbers. The equation is:—

$$\lambda = \frac{27}{64} R^2 \frac{T_k^3}{p_k^2 v_l T_l} + RT_l,$$

where λ is the molecular heat of evaporation at the temperature T_l ; v_l is the molecular volume of the liquid; p_k , T_k are the critical pressure and temperature, and R is the gas-constant.

Some thermal properties of liquid mixtures were considered from the point of view of thermodynamics.

PHYSICAL SOCIETY.

Ordinary Meeting, February 27, 1914.

Prof. Sir J. J. THOMSON, O.M., F.R.S., President, in the Chair.

THE PRESIDENT opened the meeting by calling upon Prof. G. CAREY FOSTER, who gave a short biography of Prof. Frederick Guthrie, to whom the Physical Society of London owed its initiation. Guthrie was born in 1833 and died in 1886. Like many others who had attained to distinction in Physics, he began as a chemist. He was practically the sole founder of the Society, which held its first meeting in the spring of 1874 in his own lecture theatre in the Royal School of Mines in Exhibition Road. He usually wore a grave and solemn appearance, which made him look much older than he really was, but those who knew him were aware of the warm kindness and the fund of twinkling humour which lay beneath.

Sir OLIVER LODGE said that his only claim to address them on this occasion was that he had been a student of Prof. Guthrie and also of Prof. Carey Foster. To the students Guthrie appeared a portentous senior, and he (the speaker) used to regard him as nearer eighty-five years of age than fifty. He thought it most appropriate that the Society should have inaugurated this series of lectures to commemorate its connection with Prof. Guthrie.

The PRESIDENT, in introducing Prof. R. W. WOOD, of Johns Hopkins University, Baltimore, as the first Guthrie Lecturer, referred to his unrivalled skill as an experimenter, and congratulated the Society on having obtained his services on this occasion.

Prof. R. W. WOOD then delivered the first Guthrie Lecture on "*Radiation of Gas Molecules Excited by Light.*"

The emission and absorption of light by molecules and the allied phenomenon of dispersion have led us to the conception of something within the atom which is capable of responding to light waves in much the same way as a tuning-fork responds to sound waves of the same frequency as its own, and many mathematical treatments have been built up which explain more or less perfectly many of the phenomena in question. These still leave us very much in the dark as to what is going on. Helmholtz explained absorption by introducing a frictional term into his equations of motion for the atom, and though this led at once to an expression which represented anomalous dispersion, it left us ignorant of how the energy absorbed by the molecules was transformed to heat, or how the mean

velocity of the molecules was increased by the excitation of vibrations within them. Planck avoided this difficulty by considering that the energy abstracted from the beam of light is re-emitted, though at the time the only experimental evidence was to be found in selective reflection, which occurs only in liquids and solids.

What becomes of the absorbed energy in the case of a gas? This was what he had been asking himself for many years. While he did not require a working model of the atom, he could not, however, be satisfied by an equation in which absorption was represented by a frictional term or selective reflection predicted by the occurrence of an imaginary quantity.

The problem of the constitution of the atom is one which must be approached from many sides, as it is improbable that any single mode of attack will reveal the secret. The spectroscopy alone has proved itself powerless, one great difficulty being that in all known methods of exciting spectra one got "the whole or nothing."

Flames, arcs, sparks, and vacuum-tube discharges set a host of vibrations simultaneously in operation within the atom, and resulted in a complex of lines which were difficult to interpret.

His line of attack had been to maintain the molecules in as calm and tranquil a state as possible, by keeping them cool, and then to excite them to radiation by the application of an alternating electromagnetic field of a definite frequency—usually called monochromatic light. That this method has in some degree simplified matters was proved by the fact that sodium vapour could be made to emit only one of the D lines instead of the usual two.

The conditions necessary to stimulate radiation in this way varied considerably with the nature of the element studied. He would begin, however, with the simplest case, that of a vapour which exhibits a single absorption line and emits radiations similar in every respect to the exciting radiations when stimulated by light of frequency equal to that of the absorption line. This condition was perfectly fulfilled by the vapour of mercury, which has an absorptive line at $\lambda = 2536$ in the ultra-violet.

If a beam of monochromatic light of this wave-length was focussed at the centre of an exhausted quartz bulb containing a drop of mercury at atmospheric temperature, it was found that the light was powerfully scattered by the vapour, photographs of the bulb made with a quartz lens showing the cone of rays much as if the bulb were filled with smoke. The scattered light is invariably much more homogeneous than the incident beam, in which the "line" has a finite width, whereas the scattered light corresponds only with the centre of this line. The rest gets through the vapour unaffected. With the light thus scattered—the *Resonance Radiation*—a photograph was made of a quartz bulb containing a minute drop of mercury at room temperature. The bulb appeared as if filled with ink owing to the opacity of the vapour for the rays.

These phenomena, visible only to the camera, can be visually reproduced in the case of sodium vapour excited by the light from a sodium flame. If the density of the vapour is increased by warming it, the distance which the light can penetrate into the bulb is diminished and eventually the resonance radiation is all emitted from a region so close to the surface that it appears as a bright yellow patch on the inner surface of the glass.

If this patch is now used as a lamp, and focussed by a concave mirror on the surface of the same globe (or another in which the vapour is of sufficient density to give the patch effect) so as to fall partly on a surface whitened by deposited magnesia and partly on the enclosed vapour, the brightness of the two contiguous patches thus formed is practically equal.

This proves that, under those conditions, at comparatively low densities, *true absorption does not exist*, the light abstracted from the incident beam being re-emitted as light of the same wave-length but in all directions.

The factor of true absorption makes itself manifest as soon as we admit air or some other foreign gas. Even if

the pressure is only a millimetre or two the effect is very marked.

Another point which can be brought out by this method of attack is whether or not the mechanisms whose vibration frequencies correspond to the various lines in a spectrum are independent of each other or are interconnected.

An ingenious method was described whereby a beam of considerable intensity, consisting however of only D_1 or D_2 light, could be obtained, and if the sodium vapour excited by either of these was examined spectroscopically the emitted light contained only that one of the lines which was used to excite it. This shows that the D_1 and D_2 mechanisms are quite independent. In other cases, however, vapours excited by light of any one line of their spectrum gave out a resonance spectrum of that line and one or more others showing that some groups of mechanisms were inter-dependent and could not be excited separately.

Stimulation by Waves of very Short Wave-length.—Experiments were then described in which air, nitrogen, &c., had been caused to emit ultra-violet light when exposed to the action of radiation of wave-length less than the Schumann rays, the smallest waves hitherto known. Schumann rays were completely absorbed by quartz, but would pass through a considerable thickness of fluorite, but the rays to which he referred could be reduced in intensity by 98 per cent by a plate of fluorite 1 mm. thick. Nitrogen was more actively stimulated than air by these rays, as oxygen seemed to have a destructive effect on the phenomena. Thus iodine vapour, if mixed with nitrogen, emitted a green light under the action of the rays, while remaining dark if mixed with oxygen.

He urged the necessity of an exact mathematical treatment of the phenomenon of a molecule of vapour emitting radiation which it has abstracted from an incident beam, true absorption being absent.

At the conclusion of the lecture a number of interesting experiments illustrative of the subject of the lecture were shown. These included the resonance radiation of sodium stimulated by D light, of iodine vapour stimulated by the light from a quartz mercury lamp, and of the author's method of extinguishing one of the D lines from the light from a sodium flame.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, March 4, 1914.

Mr. A. CHASTON CHAPMAN, President, in the Chair.

MESSRS. Rowland Holliday Ellis and Armand de Wael were elected Members of the Society.

Certificates were read for the first time in favour of Messrs. Lauchlan Henry Dyke Acland, 55, Comeragh Road, West Kensington, W.; Frederic Herbert Lees, 31, Summerhill Road, Dartford, Kent; William Henry Woodcock, 132, Felbrigg Road, Goodmayes, Essex; Walter Alan Gibbings, P.O. Box Sannomiya 174, Kobe, Japan.

Certificates were read for the second time in favour of Messrs. Robert Bickerstaffe, Thomas Henry Byrom, Sydney George Clifford, Donald Richard Frazer, and John McLaren.

The following papers were read:—

"Composition and Analysis of Compound Liquorice Powder." By ALBERT E. PARKES and FREDERICK MAJOR.

The authors suggest a method of chemical examination of compound liquorice powder whereby an idea may be obtained of the quality of each ingredient. Results obtained by this method from a number of commercial samples and standard samples made up from ingredients of known purity are given.

"Composition of the Saline Matter Adhering to certain Wet Salted Skins." By M. C. LAMB.

Large numbers of goat skins, primarily intended for the manufacture of glacé kid, are exported from India, which are "cured" with a natural salt earth applied to the flesh side. An analysis of the adhering saline matter shows that this consists primarily of sodium sulphate, and contains only comparatively small traces of common salt.

"Determination of Carbon Monoxide in Air." By F. S. SINNATT and B. J. CRAMER.

A method for the determination of carbon monoxide in air is described which depends upon the oxidation of the gas by means of iodine pentoxide; the carbon dioxide produced is collected in an evacuated vessel, the flow of the gas being controlled by an apparatus described by Sinnatt (*Analyst*, 1912, xxxvii., 12). The carbon dioxide present in the resulting gas is estimated by Pettenkofer's process in a similar manner to that used in air analysis.

"Standardisation of Dried Carica Papaya Juice, the Active Principal of Papain." By F. T. SHELLEY.

The method of standardisation is a slight modification of Sørensen's method of measuring the amino acids formed in an alkaline solution of pure casein. After a digestion of four hours in an incubator at 37° C., using phenolphthalein as an indicator, 0.04 gm. should produce amino acids equivalent to at least 1 cc. of N/5 alkali.

INSTITUTE OF CHEMISTRY.

At a meeting of the Institute of Chemistry held at King's College, London, on Thursday, February 26, 1914, Prof. R. Meldola, President, in the Chair, Mr. WILLIAM MACNAB delivered the first of two lectures on "*Explosives*."

He said that since the discovery of gunpowder, in the thirteenth century, man had always been trying to make explosives do work for him either for military or engineering purposes.

Whatever opinions might be held as to the use of explosives in war, there could be no difference of opinion as to the benefits reaped from the use of industrial explosives, which had lightened and expedited the work of the engineer and miner to an enormous extent.

Remarkably little alteration had been made in the composition of gunpowder, which was the explosive in practical use until about forty years ago, when cocoa or brown prismatic powder was produced to meet the requirements of the larger guns which were being made.

The discovery of guncotton had led to great hopes of more efficient explosives for guns and blasting being available, but there were so many serious accidents and it was so unreliable in its behaviour that for a number of years little progress was made. Abel first made guncotton, a really serviceable explosive, by devising the process for treating it in a paper pulping machine, which reduced the fibres of the guncotton to a very fine state of division, which enabled the acid to be thoroughly washed out and a sufficiently stable material produced.

When Nobel began to make nitro-glycerin as a blasting explosive, a new era commenced; his skill and inventiveness rapidly overcame the dangers and drawbacks which first surrounded its manufacture and use, and it had now become the main constituent of the blasting explosives most widely used.

To Vieille belonged the credit of making the first reliable smokeless powder for guns, by thoroughly gelatinizing nitro-cellulose, and Nobel succeeded in taming the two violent explosives, nitro-glycerin and nitro-cellulose, by gelatinizing them together, and producing a safe and powerful propellant. These two powders were the starting-point for all the smokeless powders subsequently produced.

The various types of other explosives were described, including the combinations of ammonium nitrate with aromatic nitro-compounds, &c., and those containing chlorates and perchlorates.

The two modes of explosion—combustion and detonation—were discussed. Gunpowder was mentioned as an instance of the first class, called a "low" explosive; in contradistinction to dynamite, which was a detonating and "high" explosive. The velocity of the explosion wave in dynamite was 6000 metres per second.

After explaining the chief principles underlying explosive reactions, the lecturer described the various methods and apparatus used in the examination and study of explosives, as well as the difficulties in controlling and retaining in vessels the products of explosion where very high temperatures and pressures of many tons to the square inch were developed.

The detonator was an important item in connection with blasting explosives, for it served to fire and develop the full force of the "high" explosive class. For many years fulminate was the chief ingredient of the detonator charge, but now trinitrotoluol, or picric acid, or tetranitromethylaniline was used as the chief ingredient, with a small priming charge of fulminate, and more recently lead azide and also tetranitroaniline had been tried.

Increased power could be obtained by the use of a detonating fuse of trinitrotoluol inserted alongside of the charge of explosive, especially in deep holes, as the trinitrotoluol detonated with greater velocity than the blasting charge, and caused it to explode more simultaneously than when ordinarily fired by a detonator placed in the top cartridge.

In the next lecture it is proposed to deal more especially with the manufacturing side of the subject, and the restrictions under which the works must be constructed and the operations carried on.

NOTICES OF BOOKS.

Allen's Commercial Organic Analysis. Volume VIII. Fourth Edition. Entirely Re-written by W. A. DAVIS, B.Sc., A.C.G.I., and SAMUEL S. SADTLER, S.B. London: J. and A. Churchill. 1914.

This volume completes the fourth edition of Allen's invaluable work, but a supplementary volume is to be issued shortly containing the latest results which have been published since the revision was first taken in hand. The eighth volume deals with the analysis of meat and milk products, proteins, and albuminoid substances, hæmoglobin and blood, proteoids and fibroids, and an introductory article by Prof. E. Frankland Armstrong on enzymes has been added. A great deal of fresh material has been incorporated in the new edition, which has undergone such extensive revision that it is practically a new work. For the sake of completeness a certain amount of matter dealing with the separation of amino acids is included, which duplicates some parts of the text of volume vii., but the editors considered it advisable to retain it in both volumes, for the information is presented to the reader from two quite different points of view.

The Art of Dying. Published by the Tapestry Studio, Shottery, Stratford-upon-Avon.

THIS is a reprint of an old book upon the art of dyeing and contains a number of recipes and directions for producing different shades upon various materials. It consists of two parts, the first of which was translated from the German, and gives "an experimental discovery of all the most useful secrets in dying silk, wool, linnen," while Part II., translated from the French, contains general instructions for the dyeing of wools and woollen manufactures. The original spelling of the first edition, published in 1705, has been preserved, and all who are interested in the history of dyeing, and the development of the art, will find the study of the book both profitable and entertaining.

A Text book of Chemistry. By WILLIAM A. NOYES. New York: Henry Holt and Co. 1913.

THE author of this book has had the requirements of two classes of college students in view, namely, those who have been through an elementary course of chemistry at school and are continuing the subject at college, and, secondly, those who are beginning the study of chemistry after having done only a little work in physics at school. The book will probably be found more useful by the former class than the latter, the order in which the subject is presented being distinctly more suitable for those to whom it is not entirely new. Thus a good deal of rather difficult theoretical work is introduced early in the text, the atomic theory being discussed at the very beginning, and catalysis, electrolysis, and the kinetic theory when only hydrogen and oxygen have been studied. Throughout the book Prof. Ostwald's device is adopted, and paragraphs dealing with more advanced subjects are marked with an asterisk. The usual ground in inorganic chemistry is, on the whole, quite adequately covered, and many examples which will give plenty of practice in calculation are included.

Radioattività ed Atomi. ("Radio-activity and Atoms"). By Prof. GIUSEPPE ODDO. Pavia: Prem. Stab. Tip. Successori Bizzoni. 1914.

THIS pamphlet contains the inaugural lecture delivered by Prof. G. Oddo before the University of Pavia at the beginning of the Academic year 1913-1914. The lecturer gave a particularly interesting account in language which was as far as possible non-technical of the history of the discovery of radio-activity and of the subsequent development of the subject. The account was thoroughly up-to-date, most recent work being noticed in it, and modern theories of the structure of the atom were tersely described. The bibliography given in the pamphlet contains the titles of all works of importance dealing with radio-activity published in English, French, German, or Italian.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 3, January 19, 1914.

Application of Spectroscopy to the Study of Chemical Equilibria. Systems formed by Oxalic Acid and Salts of Uranyl.—Victor Henri and Marc Landau.—A mixture of oxalic acid and salts of uranyl absorbs the ultra-violet rays much more than the sum of its constituents. The increase of absorption produced by oxalic acid is greater for the sulphates and nitrates of uranyl, less for the chloride, and still less for the acetate. The acetate and oxalate of uranyl absorb the ultra-violet rays more than the chloride, nitrate, and sulphate. This result confirms the general rule that the presence of two chromophore groups in a molecule produces an increase of absorption which is greater than the sum of the absorptions of each chromophore. In the present case the chromophore groups are UO_2 and COOH . There is a direct relation between the photocatalytic power of salts of uranyl and the exaltation of the absorption produced by the salts on oxalic acid.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xlvii., No. 1, 1914.

Tellurium-carbon Sulphide, CSTe .—Alfred Stock and Paul Praetorius.—By the pulverisation of electrodes of mixtures of tellurium and graphite under carbon disulphide, tellurium-carbon sulphide, CSTe , and non-volatile

decomposition products of CS_2 and also C_3S_2 , carbon subsulphide, are formed. The decomposition products are readily separated by distillation, while to free the CSTe in solution from the C_3S_2 , two methods are available:—(i.) Repeated fractional extraction of the solutions with currents of CS_2 vapours; (ii.) conversion of the C_3S_2 into a non-volatile substance and subsequent distillation. It is best to employ both methods, using β -naphthylamine as reagent in the second case. All experiments with CSTe solutions must be performed in absence of daylight or bright artificial light, as the compound and its solutions are extraordinarily sensitive to light. The melting-point of the pure substance is -54° . Its solutions are reddish brown, red, or yellow, according to their concentration. It has a characteristic smell like garlic. It is very unstable, readily giving black condensation products.

Selenium-carbon Sulphide, CSSe .—Alfred Stock and Ernst Willfroth.—Selenium-carbon sulphide, CSSe , like tellurium-carbon sulphide, can be prepared in the form of a carbon disulphide solution by the electrical pulverisation of selenium graphite electrodes under CS_2 . The C_3S_2 formed can be removed by fractional distillation in a current of CS_2 and subsequent treatment with β -naphthylamine. CSSe decomposes when exposed to light, heated, or kept for some time at room temperature. It is readily decomposed at higher temperatures, carbon diselenide not being formed.

Magnesium Chloride as Mineralising Agent, with a Contribution to the Spectro-chemistry of the Rare Earths.—K. A. Hofmann and Kurt Höschele.—Fused anhydrous magnesium chloride is an excellent solvent and crystallising agent for many inorganic oxides. Thus of the spinels magnesio ferrite, $(\text{FeO}_2)_2\text{Mg}$, is readily obtained in the crystalline form. Magnesium chloride when fused acts upon the oxides and sulphates of the coloured rare earth metals to give the crystallised oxychlorides. When the absorption spectrum of erbium oxychloride is examined it is found that it does not differ from those of the amorphous chloride and oxide. Thus the light-absorbing electrons of the erbium atom are not affected when the principal valencies are called into play by chlorine or oxygen. The same result is obtained with neodymium and praseodymium oxychlorides.

Electrolytic Reduction of Carbon Monoxide and Carbon Dioxide Dissolved under Pressure.—Franz Fischer and Oskar Prziza.—When carbon dioxide is dissolved under pressure it can be reduced quantitatively to salts of formic acid with currents of high density (10–15 amp. per sq. dm.). But high concentrations cannot be obtained because the anion of the formic acid soon begins to migrate towards the anion. With currents of low density carbon monoxide dissolved under pressure can be reduced to methyl alcohol, but the yields are poor. Methane is apparently not formed.

MEETINGS FOR THE WEEK.

- MONDAY, 16th.—Royal Society of Arts, 8. (Howard Lecture). "Surface Combustion," by Prof. W. A. Bone, F.R.S.
- TUESDAY, 17th.—Royal Institution, 3. "Modern Ships," by Prof. Sir John H. Biles, D.Sc., &c.
- WEDNESDAY, 18th.—Royal Society of Arts, 8. "House Flies and Disease," by Dr. E. H. Ross.
- THURSDAY, 19th.—Royal Institution, 3. "Heat and Cold," by Prof. C. F. Jenkin, M.A.
- Royal Society of Arts, 4.30. "Indian Water Gardens," by Mrs. Patrick Villiers-Stuart.
- Royal Society. A Discussion on "The Constitution of the Atom" will be opened by Sir Ernest Rutherford, F.R.S.
- Chemical, 8.30. "Ignition of some Gaseous Mixtures by the Electric Discharge," by H. F. Coward, C. Cooper, and J. Jacobs. "Deliquescence—Part I, The Deliquescence of Salts of Ammonium Bases," by C. J. Peddle. "Hydrazoximes of Methyl- and Phenyl-glyoxals," by B. B. Dey.
- FRIDAY, 20th.—Royal Institution, 9. "Fluid Motions," by The Rt. Hon. Lord Rayleigh, O.M., F.R.S.
- SATURDAY, 21st.—Royal Institution, 3. "Recent Discoveries in Physical Science," by Prof. Sir J. J. Thomson, O.M., F.R.S.

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or, again, $\left\{ \begin{array}{l} P = \text{soft} \\ Li = \text{hard} \\ Zn = \text{soft} \\ V = \text{hard, \&c.} \end{array} \right\} \text{relatively}$

Or, regarding the elements as metallic and non-metallic in character, these properties are seen to alternate in rows c and z ; compare the magnetic properties.

Mention should be made of the elements of the rare earth group, as it has been supposed that some of these in a pure state will be appreciably or even very strongly magnetic, judging from the relatively high susceptibilities of some of their oxides of the type R_2O_3 . The work of B. Urbain and G. Jantsch (*Comptes Rendus*, 1908, cxlvii., 1286) on these oxides indicates positive values for $k \times 10^6$ as follows: —Nd = 35.5, Sa = 6.5, Eu = 33.5, Gd = 161, Tb = 237, Dy = 290. La is diamagnetic and Pr is paramagnetic, whilst Ho has a very high susceptibility, and Er, Tu (or Tm), Ny (or Yb = Ad) and Lu (= Cp) are successively lower, the values and comparisons given being for the oxides. The two last-named elements have the values respectively, 18.3 and 3.78 for their oxides, according to S. Meyer (*Akad. Wiss. Wien. Sitz. Ber.*, 1908, cxvii., 2a, pp. 995–1000). This experimenter states that the metallic powders of Yt, Er, and Ho (mixtures) were not much more magnetic than their corresponding oxides, but they showed distinct remanence, and highly magnetic alloys may be yet possible with some of the elements of this group.

Honda and Soné (*Imp. Univ. Tôkoku Sci. Reports*, 1913, ii., No. 1, pp. 25–31), in a recent investigation on erbium (powder), find the value to be +22.4, so that this element would come next to manganese in Table II. Their investigations of the following elements will be of interest: —Diamond (dodecahedron) = 0.452; diamond (octahedron) = -0.438; sulphur (rhombic) = -0.476; sulphur (stick) = -0.444; sulphur (powder) = -0.416; manganese = +9.7 to +10.1; rubidium (regulus) = +0.088; selenium (metallic) = -0.304; osmium (powder) = +0.074; graphite (Ceylon No. 1) = -12.2 to +0.28, depending upon its axial positions, &c., in the field. At a temperature of 1200° the susceptibility of the graphite was reduced to one-fifth of its original value; on cooling below 600° it began perceptibly to decrease, and at 390° zero susceptibility was reached, which passing through the zero became $+6.8 \times 10^{-6}$ at laboratory temperature. The change at 600° corresponds roughly with the magnetic transformation temperature of iron, pointing to the presence of iron as a conditioning impurity. For diamond, graphite, sulphur, manganese, and osmium the susceptibility was independent of the field strength.

Some of the rare-earth metals, and one or two others, are arbitrarily inserted in Table IV., as a reminder that they must ultimately be dealt with in any complete scheme. Germanium in particular is arbitrarily placed. All the atomic weights of these elements are not known accurately in the first decimal place; indeed, some are not known to within nearly one whole unit. Those elements which do not appear in the special table are of high atomic weight, and they may be members of another (3rd) grouping.

The magnetic susceptibility of the weakly magnetic elements is, owing to the feebleness of the effect, profoundly influenced by the presence of impurities, such as iron, and no doubt the physical state of the substance (see carbon) is also a factor which sometimes renders the values in question in some degree uncertain, or unsatisfactory for close comparative purposes. In these tables many of the values were obtained by Honda (in co-operation with H. E. J. G. du Bois), and for purposes of comparison such values may be given a preference (see Honda, *Ann. Physik.*, 1910, xxxii., 1027). In the Landolt-Börnstein compilation references are given, and for a detailed study of the subject the original papers should be consulted.

Chemical Society.—The Annual General Meeting of the Chemical Society will be held on Thursday, March 26, 1914, at 4.30 p.m., when the President (Prof. W. H. Perkin, F.R.S.) will deliver his Address, entitled "Recent Researches on Tautomerism."

THE DETECTION OF TRACES OF COPPER.*

By WESLEY B. PRITZ, A. GUILLAUMEU, and
JAMES R. WITHROW.

A FREQUENT feeling of uncertainty regarding the significance of qualitative tests for the completeness of the electrolytic precipitation of copper, made it desirable to know the limits of the sensitiveness of the recommended reagents, as commonly employed. It was also desired to modify, if necessary, the sensitiveness of one of the reagents to meet the requirements of the work on electrolytic precipitation of copper in progress in the Chemical Laboratory of the Ohio University. As it is often essential in electro-analysis to remove only such volume of solution for the qualitative test as will contain an insignificant weight of copper, the method selected must be made applicable to samples not greater than about 1 cc. Of the reagents recommended, the ones which in our experience are in most general use are ammonium hydroxide, ammonium sulphide, and potassium ferrocyanide. Since a study of the sensitiveness of these three, under the conditions in the copper work on hand, showed that ferrocyanide could be made to answer our purpose, other methods were not examined.

Heine appears to have utilised colour for the detection of copper as early as 1830 (*Bergwerksfreund*, i. 33; xvii., 405; *Zeit. Anal. Chem.*, xvi., 644). Müller, in 1855, with his complement colorimeter using 5 cc. of solution was able to detect 50 parts of copper in 1,000,000, using ammonium hydroxide as reagent (*Journ. Prakt. Chem.*, lvi., 203). Wagner, in 1881, stated that the blue colour given to solutions of copper salts by ammonium hydroxide will detect 1 part in 25,000 (*Zeit. Anal. Chem.*, xx., 351). Milbauer and Stänek, in 1907, thoroughly investigated this colour, and found that free ammonia and ammonium chloride diminished the intensity, but ammonium carbonate intensified it one-third (*Zeit. Anal. Chem.*, xvi., 644).

Carnelley, in 1875, found that in acid solution, ferrocyanide will detect 1 part of copper in 1,000,000 parts of water, while in neutral solution the colour changes from brown to brown purple, and 1 part copper can be detected in 1,500,000 parts (*CHEMICAL NEWS*, xxxii., 308). The addition of ammonium nitrate or any other ammonium salt greatly increases the depth of colour, making possible the detection of 1 part of copper in 2,500,000 parts. Hydrogen sulphide is also said to detect 1 part of copper in 2,500,000 parts of water. Wagner, in 1881, reported that ferrocyanide will detect 1 part of copper in 200,000 parts of solution (*Zeit. Anal. Chem.*, xx., 349). Nessler and Barth, in 1883, used 10 cc. of solution, and could detect 2 parts in 1,000,000 with the use of potassium ferrocyanide (*Zeit. Anal. Chem.*, xxii., 37). Cooper, in 1886, by using varying depths of solution up to 14½ inches in tubes enclosed in opaque cylinders, claims ability to detect 1 part of copper in 1,950,000 parts of water with ammonium hydroxide, and 1 part in 11,750,000 parts with ferrocyanide (*Journ. Soc. Chem. Ind.*, v., 84). H. Thoms, in 1894, placed the limit of this last test at 1 part in 200,000 (*Pharm. Centralhalle*, xxxi., 31; *Zeit. Anal. Chem.*, xxxiii., 464). Bradley, in 1906, found that potassium ferrocyanide could detect copper in a solution containing 1 part in 100,000, but not in a solution of 1 part per 1,000,000 (*CHEMICAL NEWS*, xciv., 189).

Such variation in values for the sensitiveness of the reagents mentioned should surely meet any requirements which might arise. We made no attempt to reconcile or judge between any of them, except in so far as our own conditions were concerned. Many other tests have been advanced from time to time, and doubtless have much value in their place. The range of recommendation even in this kind of work is quite broad, but from our point of view somewhat lax. Such tests as raising the level to see

* Read before the Indianapolis meeting of the American Chemical Society. From the *Journal of the American Chemical Society*, xxxv., No. 2.

if fresh copper is deposited (Treadwell-Hall, "Analytical Chemistry," 1905, vol. ii., p. 148; Fresenius-Cohn, "Quantitative Chemical Analysis," 1908, p. 621; Low, "Technical Methods of Ore Analysis," 1908, p. 89; Julian, "Quantitative Chemical Analysis," p. 250; Warwick, *Zeit. Anorg. Chem.*, i., 289), and electrolysing until the solution becomes colourless (Rudörf, *Ber.*, xxi., 3050), do very well in many cases, but frequently are inadequate. We have noticed, for instance, in cases where the test used was the raising of the level of the electrolyte toward the end of a precipitation between insoluble electrodes, and no visible copper was deposited, that there was a sensible lowering of the intensity of the ferrocyanide test made before and then after the rise in level.

Experimental.—The stock solutions used contained 1 part of copper as sulphate in 1000, and also in 25,000 parts. The copper sulphate was "Baker's Analysed" in the last case and iron-free crystals re-crystallised after several precipitations as crystal meal in the other case. In the preliminary experiments, when 1 cc. portions of solution were examined in ordinary test-tubes, the conservative statements in the literature regarding sensibility were confirmed, although somewhat greater sensitiveness could be obtained. In the case of ammonium hydroxide 1 part of copper in 40,000 could be detected, but not with as great certainty as 1 in 25,000. With potassium ferrocyanide in presence of acetic acid the sensitiveness varied roughly inversely as the concentration of the ferrocyanide solution used. One drop of 8.5 per cent ferrocyanide added to 5 cc. of solution in an ordinary test-tube could detect 1 part of copper in 200,000 parts of solution, but not in 300,000 parts. A 3 per cent solution of ferrocyanide added in the same way to 1 cc. portions gave a distinct pink, with a dilution of 1 part in 300,000 and not with 1 in 600,000. The same results were obtained using 2 cc. portions. These results were not as delicate as desired. It was found, too, that slight variations in the procedure when making and examining the tests gave pronounced differences in results. This doubtless has a bearing on the widely varying values on record. In fact, a study of the literature seems to indicate that a major factor in the variations in the recorded values is the lack of uniformity in the quantity of sample used. In our work means of regulating other factors causing difficulty were developed.

Apparatus.—The apparatus finally adopted for detecting traces of copper was an adaptation of the ordinary Nessler tube, and was exceedingly simple. A number of tubes were made, 3 to 5 mm. in internal diameter and up to 15 cm. in length, having a capacity of nearly 3 cc. They were made from ordinary thin-walled glass tubing, one end being sealed and preferably slightly ballooned to avoid thickening. The glass used was the lightest obtainable. When viewed on the end it must not be green, or the delicacy of the tests will be affected. The side-walls of the tubes were wrapped with black paper to exclude all light except that entering the bottom of the tube. This wrapping greatly increased the delicacy of the tests on the weaker solutions. The solution to be tested was introduced into the tube by means of a 1 cc. pipette.

Ammonium Hydroxide Reagent.—Three drops of this reagent (sp. gr. 0.904) were added to the 1 cc. of the solution to be tested, contained in a tube. A blank containing 1 cc. of distilled water and three drops of the hydroxide was also prepared in each case. The two tubes were observed in light thrown up through them from a white screen. N/2500 copper sulphate solution gave an easily distinguishable coloration; with N/3000 the colour was faintly distinguishable, while with N/4000 it could scarcely be distinguished at all. N/3000 was therefore taken as the limit of the sensibility of ammonium hydroxide in the detection of copper in sulphate solutions in such tubes as described. This means that in 1 cc. of electrolyte tested copper may still be detected with the ammonium hydroxide reagent when the electrolyte contains 0.00106 gm. of copper per 100 cc. or 10.6 parts per 1,000,000. This is

too much copper to leave in the electrolyte when a gm. or less of copper is being deposited.

Ammonium Sulphide Reagent.—This reagent was made in the usual manner and used as the ammonium hydroxide just described. Solutions as dilute as N/20,000 gave evidence of the presence of copper. The colour from N/25,000 solutions could scarcely be differentiated from that of the blank comparison tube. N/20,000 was therefore established as the practical limit of sensibility with ammonium sulphide. This means 0.00016 gm. copper per 100 cc. of solution when 1 cc. of the solution is used in the test, or 1.6 parts per 1,000,000. This sensibility was in close agreement with the error in weighing of the work under way, and would therefore have been satisfactory had it not been found that the reagent must practically be made fresh on the day it is used or the results are not dependable. The reagent decreases in sensitiveness. After six days' standing in a stoppered bottle, in one case, the reagent failed to detect any copper in an N/5000 solution. One week later copper could scarcely be detected in an N/1000 solution, with the original reagent. The addition of ammonium hydroxide to reduce the yellow colour assumed by the deteriorated ammonium sulphide reagent did not seem to improve its sensibility. The work on ferrocyanide resulted so satisfactorily that the ammonium sulphide deterioration was not further investigated.

Potassium Ferrocyanide Reagent.—This reagent gave the best satisfaction. It is in quite common use, but is frequently erroneously thought to be entirely too delicate. It was prepared by dissolving 1 gm. of Baker's chemically pure ferrocyanide in 50 cc. of water. This was amply strong to precipitate the copper, and not so coloured as to interfere greatly with the delicacy of the test. A pinkish brown colour was obtained with the dilutions of copper salt used. Three drops of the reagent were used, and the tests conducted as described above. The copper in N/20,000 solution could easily be detected by this reagent, but the colour difference became less and less marked as dilution took place. At a dilution of N/35,000 the colour difference (compared with the blank) was just discernible. This was therefore the limiting sensibility, and indicates the presence of 0.00009 gm. of copper in 100 cc. when 1 cc. is used in the test, or 0.91 part per 1,000,000. This is not quite twice as delicate as the test with fresh ammonium sulphide. It is much more delicate than when the test is performed with a drop of the solution on white porcelain, even when the ferrocyanide is as dilute as 0.1 per cent.

Influence of Reagents.—The influence of the proportions of the reagent and its auxiliaries as well as other substances was studied in the case of potassium ferrocyanide by means of Nessler tubes in 50 cc. portions. The tubes were wrapped with black paper. Difficulty was at first experienced in using the ferrocyanide test on samples from a nitric acid electrolyte. This was caused by a yellowish green coloration which formed in the tube containing the electrolyte, masking any pink colour which be produced. Sometimes the pink which appeared was at once superseded by the green colour. The interfering colour did not seem to appear in samples containing a negligible amount of copper (0.1 mgrm. or less in 125 cc.). The addition of 2 per cent of nitric acid to the ferrocyanide-copper nitrate mixture produced cloudiness, interfering with the delicacy of the test. Acetic acid, on the other hand, did not interfere, and really produced a better coloration. Ammonium hydroxide seemed to destroy the copper ferrocyanide colour, and gave a colourless to a green colour when in excess. The addition of an acid brought this colour out again. An excess of potassium ferrocyanide affects the delicacy of the test in that it changes from pink to yellow, thereby slightly decreasing the delicacy. Ammonium nitrate increases the delicacy of the test. Excess of acetic acid is of little influence. Ammonium acetate has no effect.

Interference of other Metals.—Zinc has no effect on the

delicacy of the ammonium hydroxide reagent when sufficient excess is added and time allowed to re dissolve the hydroxide first precipitated. This is true even when a very great excess of zinc is present, such as would obtain when 10, 20, 30, and 40 per cent alloys of zinc with copper in 1 grm. quantities were dissolved in 100 cc. and the copper reduced in amount until it was N/3000. These are the practical conditions met with in the electrolytic separation of copper from zinc.

N/35,000 copper solutions containing the excess in amounts of zinc just mentioned gave very unsatisfactory results with ferrocyanide, however, because of the precipitation of zinc ferrocyanide. This reagent was therefore useless in the presence of zinc.

Conclusions.—I. The contradictory state of the literature indicates that results in colorimetric examinations are not comparable unless the volumes worked with and the diameter of the apparatus used are at least approximately known.

II. It has been found with the method used that the end-point of an electrolytic precipitation of copper, no other metals being present, may be detected by—

Ammonium hydroxide with an error not greater than 0.105 per cent;

Ammonium sulphide with an error not greater than 0.015 per cent;

Potassium ferrocyanide with an error not greater than 0.009 per cent;

provided the volume of the electrolyte was 100 cc., and there was originally present 1 grm. of copper.

III. The recommended procedure for the detection of traces of copper at the end of electrolytic copper precipitation in the kinds of solutions indicated, is as follows:—Take 1 cc. of the sample in a narrow test-tube constructed as described. Make alkaline with ammonium hydroxide, acidify with glacial acetic acid, and add 2 drops of 2 per cent $K_4Fe(CN)_6$ solution. A pronounced red colour indicates more than 1 mgrm. of copper. Make similar additions to another tube as a blank, replacing the sample to be tested by distilled water. If by comparison the tubes are practically of the same colour, then there is present not more than 0.1 mgrm. of copper in 100 cc. of the solution.

NATIONALISATION OF SOURCES OF RADIUM IN UNITED STATES.

REPORT OF COMMITTEE ON MINES AND MINING.

THE Committee appointed to consider the question of securing an adequate supply of radium for the use of the Government and people of the United States began on January 19, 1914, to hold public hearings for the purpose of obtaining information on the subject from those in favour as well as from those opposed. The Committee gave six days to the hearings, and gave full opportunity for those interested to appear and testify. As a result of these hearings the Committee recommended that a Bill be passed to provide for and encourage the prospecting, mining, and treatment of radium-bearing ores in lands belonging to the United States, for the purpose of securing an adequate supply of radium for Government and other hospitals in the United States, and for other purposes. This Bill gives to the General Government a preferential right to purchase the radium-bearing ores from lands now owned by the Government, at such prices to be fixed by the Secretary of the Interior as will cover the cost of and encourage mining operations, and under conditions that require the full and prompt development of the radium deposits for the benefit of the people. At the same time it furnishes to the actual prospector or miner a steady market for his ores and sure and prompt payment for the material when sold—two conditions that he has not always enjoyed in the past. The Bill safeguards the interests of all the people, and provides for any unforeseen conditions by authorising the Secretary

of the Interior to fix semi-annually the price to be paid for the ores under conditions that will insure the prospecting for and mining of them; allows the Secretary to permit the sale and delivery of these ores after or without tender to the United States, if conditions arise which make this advisable, *i.e.*, if conditions arise under which the Government is for a time unprepared to purchase the ores; and it permits him to accept or purchase radium-bearing ores from deposits already in the hands of private individuals, should such tenders be made and the material be needed. It also authorises him to dispose of the radium extracted under conditions that will best serve the needs of the people of the United States, keeping in mind always the needs of the many who are unable to bear the burden of expensive journeys or costly treatment which now limit such treatment to the few. It authorises an appropriation to cover the cost of the mining of the radium-bearing ores on the public lands and the extraction of the radium. If such policy is deemed wise the Secretary of the Interior may sell a part or all of the radium produced to American hospitals at cost of production and turn the receipts therefrom into the Treasury, thus reimbursing the Government in part or in full for the expenditures under this act.

From information brought before it the Committee is convinced of the great public need of the legislation herein proposed. It has been shown by the highest medical authority and to the Committee's satisfaction that radium is a cure for certain forms of cancer, particularly those of an external nature which have not progressed beyond the reach of this or any other remedy; that it is almost a specific in certain forms of giant sarcoma; and that many cases of cancer quite beyond the hope of surgery can be and have been cured by this agent. From the evidence at hand it seems probable that by the use of larger quantities of radium than are now available, a large number of present failures might be transformed into cures. Unfortunately up to the present time no American surgeon has been able to procure for use in any case more than 1 grm. of radium, and the total quantity now available for all American hospitals does not exceed 2 grms.

As there are estimated to be over 200,000 cases of cancer in the United States, and 75,000 people yearly are said to die of cancer, the importance of this discovery and the seriousness of this situation for the American people cannot be overestimated. It has been shown to the satisfaction of the Committee that during the last two or three years the United States has supplied from two to three times as much of the raw material used in producing radium as all the rest of the world together; that this material has for the main part been exported to foreign countries at prices entirely incommensurate with the actual value of the contained radium; that up to January 1, 1914, only 2 grms. of this material had been produced in the United States; and that one company—the only company in the United States now actually producing and selling this material—has already contracted abroad for the major part of its 1914 output. It has also been shown that on account of the great foreign demand for the material it is practically impossible to procure radium at any price for immediate delivery, and that when future deliveries are promised the price is so high and so far beyond the actual cost of production that there is small hope that this remedy will become generally available for rich and poor alike in the United States.

The Committee is therefore convinced that Congress should immediately take steps, as proposed in this bill, to develop the radium resources still belonging to the people of the country, and to do this under conditions that will secure and make immediately and widely available the largest possible supply of this radium for the treatment of the sufferers from cancer among the people of the United States. The Bill now reported will accomplish this purpose in a manner which, it is believed, instead of discouraging will encourage and stimulate the prospector to discover and mine the radium ore deposits by giving him a certain and fair reward for his discovery and his work.

Resources.

Radium ores are known to occur in several localities, but always in comparatively small amounts. The richest radium-bearing region is undoubtedly the Paradox Valley region in Montrose County, Colo., where the ore is carnotite, containing uranium and vanadium besides radium. Mines at Joachimsthal, Austria, have been taken over by the Austrian Government, and are being developed through governmental resources. The only ore there is pitchblende, an impure oxide of uranium carrying radium. Pitchblende is also found in Gilpin County, Colo., whence several tons of ore have been shipped abroad to contribute a little to the radium supply.

In the old tin-mining district in Cornwall, England, some pitchblende is also found, and an English company and one of the French companies are reputed to get their chief supplies from low-grade ores on the dumps and in the stopes of the old tin mines.

Deposits of autunite, another radium-bearing mineral, are known to occur in Portugal and also in Australia, and a few hundred milligrams of radium are yearly produced from these ores. Carnotite is, however, the chief source of radium at present. Very low-grade deposits of carnotite mixed with another mineral (ilmenite) are known to occur in Australia, and a plant has been started in that country which is producing from 100 to 200 mgrms. of radium per month. A deposit has also been found at Ferghana, Russian Turkestan. It has not yet become a regular source of supply, and there is no reason to believe, from any report issued up to the present time, that it will prove a large source of radium. In fact, no deposit of radium ores anywhere discovered gives any promise of supplying material enough to meet the immediate demands.

The carnotite deposits of Colorado and Utah are, as before stated, the most extensive in the world. They have, however, been very wastefully exploited, some 4 tons more or less of low-grade ore having been thrown on the dumps or mixed with mine waste for every ton of shippable ore so far marketed.

Present Ore Supplies.

According to the testimony presented to the Committee from 700 to 1000 claims have been at one time or another staked in Colorado and Utah; of these claims perhaps 300 may eventually be worked and 150 may be considered reasonably good. These claims have been for the main part bought up by a few interests, and for only a few claims has the prospector obtained more than 50 dols. to 200 dols. a claim. The Standard Chemical Co., of Pittsburgh, controls approximately 170 of these claims; the General Vanadium Co., of Liverpool, England, 58; the Radium Co., of America, 20 to 25; Thomas F. Curran, 70 or more; O. B. Wilmarth, 20 to 25; and the National Radium Institute, 16. The others are scattered among the smaller producers. Many claims are being located at present, and if a supply of radium is to be preserved for America prompt action by Congress is necessary.

Future Ore Supplies.

As to future ore supplies no definite statements can be made, the testimony presented to the Committee being contradictory. Those who now own claims are very sure that other supplies will be found in quantity. There is no reason to believe that further discoveries will not be made, although the mining engineers reporting to the Denver Chamber of Commerce, the employees of the Bureau of Mines, and members of the Geological Survey state that all known deposits are already located. Accordingly it will probably be necessary, if the Government is to secure immediate supplies, to purchase from owners of claims already located, as well as to put forth every effort to open up new deposits.

The carnotite region is known to be extensive, there being an area of something over 480,000 acres within which pockets of carnotite are apt to occur. But in many places the carnotite-bearing stratum has been eroded away,

and in many others it is so deeply buried by later beds that there is no reasonable hope of ever obtaining the supplies that are undoubtedly embedded therein. There are, however, certain areas where this stratum is only a few feet under the surface, as well as many places on the canyon sides where it outcrops and where pockets of carnotite are likely to be found. These carnotite deposits, however, are mainly small, no claim having yet produced without exhaustion more than 500 tons of shippable ore. Most of the pockets contain less than 50 tons. These pockets are not connected by stringers, and there is no evidence of vein formation. Accordingly the finding of one pocket is no indication that others are adjacent, although sometimes this may be the case. With the large number of prospectors now in the field it is hoped and expected that new discoveries will be made, and that sufficient bodies of ore will be opened up to assure the radium necessary for American hospitals.

Saving of Waste.

Many of the claims already worked have on their dumps considerable quantities of ore that is too poor to ship at such prices as have prevailed in the past. There is every reason to believe, however, that concentration methods can be developed by which much of this ore can be concentrated on a basis that will make a large part of it available for use. This is a very important work for the Government to do, as more than twice as much radium has been wasted as has actually found its way to market. Certainly every effort should be made to conserve this almost priceless material.

United States Production and Exportation.

As in most radium ores there is a fairly definite ratio of radium to uranium (1 to 3,000,000), the amount of radium obtained and exported can be roughly calculated from the uranium content of the ores sold. According to the figures of the Bureau of Mines, carnotite ores carrying 28.8 tons of uranium oxide were produced in 1912, and practically the entire amount was exported. In that year the uranium content of the major part ran between 2 and 3 per cent of uranium oxide, as, owing to the cost of transportation, no ore carrying less than 2 per cent could be marketed. From the ores shipped abroad in 1912, 11.43 grms. of anhydrous radium bromide could have been and probably were extracted. In 1913, according to preliminary figures of the United States Geological Survey, 2140 tons of ore were produced, of which 1198 tons were shipped to works in this country and 942 tons were exported. However, owing to the cost of transportation only the richer ores were exported, so that radium equivalent to about 7.5 grms. of anhydrous radium bromide, more than one-half of the total American production for the year, was sent abroad. One foreign company did not work its plant in the Paradox Valley, Colo., during the greater part of the year, because it was building a new plant in Liverpool, and it cost less to leave the ore in the mine than to take out the ore and store it in England. This company will be a large exporter of carnotite from Colorado and Utah during 1914.

It is improbable that all of the ores exported are now represented by finished product, but the actual production for 1912 and 1913 cannot be much less than the quantity mentioned. The total quantity of uranium exported in 1911 was almost equal to that exported in 1912, and ores are still being sold for treatment abroad. There can be no doubt that in 1912 and 1913 there was obtained from American ores more than twice and probably three times as much radium as from all other sources combined.

The carnotite prospects and mines of the West have been described in *Bulletin 70* of the Bureau of Mines, and the subject is further treated in "Advance Chapters from Mineral Resources for 1912," by F. L. Hess, of the United States Geological Survey. The mines are for the main part in Montrose and San Miguel Counties, Colo., and in a somewhat more extensive territory just to the west and north-west of these deposits in Utah. Since *Bulletin 70*

was written, prospecting in this region has been extensive. Many agents of foreign manufacturers have been in the country seeking supplies for shipment abroad, and a much stronger demand for ores has caused prices to advance, so that at present ore containing 2 per cent of uranium oxide readily brings 80 dols. per ton at the railroad at Placeville, Col. Correspondingly higher prices are obtained abroad, and some private producers who were able to contract for considerable quantities report even higher prices.

Owing to the interest aroused and to the proposed withdrawal of radium-bearing lands there has been a decided increase in prospecting, and some important new finds have been made. Although many claims have been staked in different parts of the radium-bearing region, the most important finds have been at the summit of Big Canyon at the head of Lisbon Valley, Utah, just across the State line from the McIntyre district, Colorado. Other important finds are reported in the Henry Mountains, about 100 miles south-east of Green River, and in a district about 7 miles north-east of Monticello, Utah. Development work has been carried on at Gateway and also in the western part of the Paradox Valley, the original scene of the main operations.

(To be continued).

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

A FOSSIL GAS A HUNDRED MILLIONS OF YEARS OLD.

The question of the presence in the atmosphere and of the origin of the five rare gases at present known—helium, neon, argon, krypton, and xenon—is one of the most interesting features of modern science. In particular, helium, which exists in all hot springs and results from the disintegration of the radioactive substances in the bowels of the earth, contributes in keeping up the radioactivity of the atmosphere by the permanent emission of penetrating atoms, electrified, moved by a prodigious speed, and capable of playing an important though still imprecised rôle in the functional acts of life. Prof. Moureu, in collaboration with M. Lepape, has just informed the Academy of Sciences that coal damp constantly contains, in company with other rare gases, enormous proportions of helium. It is thus that the mine of Frankenholz, in Westphalia, pours out into the atmosphere as much as 4000 cubic metres of helium a year. However, coal possesses only very small quantities of radium and thorium incapable of explaining the production of so much helium. It is thus certain, in these conditions, that the abundant helium of coal-damp is, for the far greater part, fossil helium, dating from the carboniferous period, which enables its age to be reckoned at from 50 to 100 millions of years!

THE FIRST THESIS FOR THE DOCTOR'S DEGREE IN PEDOLOGICAL SCIENCE.

This title has just been conferred for the first time by the International Faculty of Pedagogy of Brussels, 69, rue de la Culture, directed by the lady doctor J. Totevko. This faculty has grouped together all the disciplines concerning the scientific knowledge of children, without forgetting the practical applications of Pedagogy, and it has raised pedagogy to the dignity of a real science able to fill the programme of a university course of teaching. Considered from this point of view, the crowning of the pedagogical studies necessarily includes the accomplishment of an original work; that is to say, the composition of a thesis for the doctor's degree. The first to receive this degree is M^{me}. Lifoka-Librach, who after three years' experimental study pursued in the school of Brussels on 420 school children, has succeeded in drawing up a work of more than 120 pages, entitled, "On the Relations between Sensorial Acuity and the Development of the Intel-

ligence." M^{me}. Librach has managed to obtain a very strict correlation between the intelligence of children and the fineness of their senses. It is a truth of a statistical order. The relation sought for appears more distinct for young children of nine or ten years than for those who are nearing the end of their primary studies. The work contains a great number of applications specially interesting for pedagogy.

LIGHTING BY NEON TUBES.

Neon is one of the five rare gases contained in the atmosphere. Its applications for lighting purposes are very curious. Prof. d'Arsonval has presented before the Academy a work of M. George Claude, showing that large neon tubes are not superior to small ones, for the production of light in these tubes depends on the product of the volts by the ampères, that is to say, on the force expended. On the contrary, the luminous production remains excellent, and of the rank of half a watt per candle, down to very small diameters, 10 mm. and less. It becomes then easy to make very short tubes, exceedingly easy to manipulate, giving a very weak luminous force, with an excellent production, which had been impossible up till now for lighting by luminescence.

HOW OCEANS ARE FORMED.

M. Fermier has presented a paper by M. Emile Belot on the "Physical Laws of the Formation of Primitive Oceans and Continents." On the Earth and on Mars oceans dominate greatly in the austral hemisphere. Th's fact may be attributed to the translation in the south-northerly direction of these planets in the primitive nebula. The friction of this nebula on the exterior surface of the planetary atmosphere determines a north-southerly circulation, which is completed on the surface of the condensed nucleus by a south-northerly circulation. It is then around the antarctic that cold vertical currents can reach the nucleus and that the temperature can at first be inferior to 364° (the critical temperature of water). The condensation of the oceans is then produced around the South Pole, determining currents towards the Equator, which explain the formation into a point, towards the south, of the austral continents. The calculation, founded on the permanent regime of the speeds of these currents and of the solid matter that they transport, is verified by direct measures—thus, below sea-level 2000 metres the breadth of the oceans is constant on the parallels of the austral hemisphere, and the breadth of the continents is constant on the parallels of the boreal hemisphere.

NEW METHOD OF ANALYSING DRINKING WATER.

Prof. Moureu has shown, according to M. Halméjac, of Bordeaux, that the richness of waters in chlorides is proportional not only to the organic matters but to the microbian germs that these waters contain. Whence is to be derived the possibility of appreciating, by a simple determination of the chlorides, whether a water is fit for drinking or not.

THE SIGNS OF FATIGUE.

With a view of determining the methods of scientifically regulating labour and work, M. J. M. Lahy, in a paper presented by M. Edmond Perrier, director of the Paris Natural History Museum, has fixed the means of recognising the objective signs of fatigue in the so-called modern professions which do not require great muscular effort. Experiments carried out by him in 1903 on the postmen employed in the railway postal vans, on printers, linotypists, and type writers, have given concordant results. The signs of fatigue in these workers are constituted by an increase of the pressure of the blood and by a slackening of the time of reaction.

THE TRANSMISSION OF HERTZIAN WAVES.

MM. Prosper and Rothi have sought to verify the variations of the transmission of the Hertzian waves according to the state of the atmosphere. Prof. Bouty,

who has informed the Academy of their studies, confirms the preceding researches. The transmission of the waves of Hertz takes place better in the night than in the day.

THE ALTERATION OF SPEECH BY MICROPHONES.

For some time past there have been attempts made to utilise the oscillographic study of microphonic currents to analyse the sounds of the voice and to improve telephonic transmission. But the diagrams thus taken off by different experimenters, and which were thought to be comparable, at least as far as the transcription of vowels was concerned, have now been recognised as discordant. This fact has led M. A. Blondel and M. Polak to take the question up again, following a method which utilised the Blondel oscillography. They explain this method in the *Annales des Postes, Telegraphes, et Téléphones* of December last. It appears from this that microphones can introduce their own oscillations, which are of independent frequency to that of the voice, when their membranes or granules of carbon are not deadened or slackened. But, on the other hand, an excess of padding or deadening may stifle certain sounds. The granulated microphones give many parasitical vibrations. The authors have merely enregistered diagrams of vowels, without going into the study of consonants, which are still more complex and more liable to deformation.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 5, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

Papers were read as follows:—

"Action of Light on Chlorophyll." By HAROLD WAGER, F.R.S.

When chlorophyll is decomposed by light, at least two distinct substances are formed, one of which is an aldehyde or mixture of aldehydes and the other an active oxidising agent, capable of bringing about the liberation of iodine from potassium iodide. This can be demonstrated in various ways.

The decomposition of chlorophyll appears to be due directly to the action of light and is not an after effect of the photo-synthesis of carbon dioxide and water. It takes place only in the presence of oxygen, and it appears to be a case of photo-oxidation, for oxygen is used up so completely in the process that chlorophyll can be used instead of pyrogallol and caustic potash to determine the amount of oxygen in a given amount of air. In the absence of oxygen no bleaching takes place. Carbon dioxide is not necessary to the photo-decomposition of chlorophyll and is not used up in the process, even when present in considerable quantities. The bleaching of chlorophyll takes place just as rapidly and completely in its absence as in its presence, and the same two substances are produced. Formaldehyde appears to be formed in small quantities, but the main bulk of the aldehyde produced by the photo-decomposition of chlorophyll is not formaldehyde. The oxidising substance does not give the reactions for hydrogen peroxide; it is possibly an organic peroxide.

The decomposition of chlorophyll and the production of aldehyde is also brought about by the action of oxidising agents such as hydrogen peroxide and permanganate of potash. This may take place in the dark very rapidly in the case of permanganate of potash, but very slowly in the case of hydrogen peroxide. In the light the oxidation due to hydrogen peroxide is, however, much accelerated.

The bleaching of chlorophyll *in situ* in green leaves gives the same products as the chlorophyll extracts outside the plant.

"Formaldehyde as an Oxidation Product of Chlorophyll Extracts." By C. H. WARNER.

"Controlling Influence of Carbon Dioxide in the Maturation, Dormancy, and Germination of Seeds." By FRANKLIN KIDD.

Experiments are described showing that germination of seeds can be completely inhibited by carbon dioxide in the atmosphere (20–30 per cent, varying with the temperatures used). This inhibition is not accompanied by injury. The seeds germinate at once after removal from inhibitory CO₂ pressures.

In one case (*Brassica alba*) a still more striking result is obtained. Inhibition is not terminated by removal of the seeds from the CO₂ pressures to air, but continues indefinitely, though the seeds lie in well aerated and moist conditions, at 15°–20° C. This condition of continued dormancy in the face of a favourable environment for germination is at once suggestive of cases of "delayed germination" often met with in nature, where seeds do not germinate but lie indefinitely in soil in apparently good germinating conditions.

This continued inhibition of *Brassica* seeds when removed from atmospheres containing CO₂ to air is found to be terminated by removal of the testas, or by complete drying and re-wetting of the seeds.

The conclusion indicated is that a change in the testa rendering it less permeable to gases is produced by the action of CO₂, whereby after removal of the seeds to air the CO₂ produced in the embryo will be to an increased degree held up in the tissue, while at the same time the amount of oxygen penetrating the testa from the atmosphere will be lowered. The seed is thus sealed by its testa for a long period of dormancy under the influence of carbon dioxide.

Experiments in the field showed that this action of CO₂ may actually occur in nature. If a quantity of green plant material is buried deep in the ground, seeds planted in the soil over this decaying material are inhibited in their germination by the CO₂ produced beneath them. This is of agricultural significance, and the fact that in the case of mustard seeds suspension of vitality continues even after the external CO₂ has been removed, suggests an explanation of the common occurrence of dormant seeds of this plant in fields, and possibly of other natural cases of delayed germination.

"Functional Correlation between the Ovaries, Uterus, and Mammary Glands in the Rabbit: with Observations on the Estrous Cycle." By J. HAMMOND and F. H. A. MARSHALL.

"The Chromaffine Systems of Annelids and the Relation of this System to the Contractile Vascular System in the Leech, *Hirudo medicinalis*." By J. F. GASKELL, M.D.

CHEMICAL SOCIETY.

Ordinary Meeting, March 5, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

MESSRS. E. E. Turner, John K. Wood, A. Bramley, Bertram Campbell, and Ivan R. Gibbs were formally admitted Fellows of the Chemical Society.

The names of the Fellows recommended by the Council for election as official and ordinary Members of Council, 1914–1915, were read from the Chair.

The PRESIDENT announced that the Rooms of the Society will be open for an informal meeting of the Fellows on Thursday, April 30th, from 8 to 10 p.m. Smoking will be permitted, and light refreshments will be provided. Fellows are invited to exhibit apparatus and specimens of interest, and to show experiments, and those wishing to do so are requested to communicate with the Honorary Secretaries not later than the Monday previous to the meeting.

It was also stated that a meeting of the Faraday Society will be held in the Rooms of the Chemical Society on Friday, March 27th, 1914, when a general discussion on "Optical Rotatory Power" will take place. Fellows of the Chemical Society are invited to attend. The meeting will be held from 5 to 6.30 p.m., and from 8 to 9.30 p.m., tea being served at 4.30. Further particulars can be obtained from the Secretary of the Faraday Society, 82, Victoria Street, S.W.

Certificates were read for the first time in favour of Messrs. Raymond Foss Bacon, B.Sc., Ph.D., Mellon Institute of Industrial Research, University, Pittsburgh, Pa., U.S.A.; Robert Reginald Baxter, B.A., St. John's College, Oxford; Brojendranath Ghosh, M.Sc., 59, Hereford Road, Bayswater, W.; Richard Selwyn Haskew, Cwmbran, Newport, Mon.; Ralph Waldo Emerson MacIvor, 47, Victoria Street, Westminster, S.W.; Henry Ratcliffe, 38, Sefton Terrace, Beeston Hill, Leeds; John Rogers, 195, West George Street, Glasgow; Percy Charles Rundell, Glenhorne, St. Albans Crescent, Woodford Green; Max Herbert Tagg, B.Sc., Brentor, Clayton Avenue, Wembley; Albert Watkins Maggs Wintle, Holly House, Saltcoats, Ayrshire.

Of the following papers those marked * were read:—

*59. "The Atomic Weight of Vanadium." By HENRY VINCENT AIRD BRISCOE and HARRY FRANK VICTOR LITTLE.

The ratios $\text{VOCl}_3 : 3\text{Ag}$ and $\text{VOCl}_3 : 3\text{AgCl}$ have been re-determined. Vanadyl trichloride was decomposed by aqueous ammonia, acidified with nitric acid, and the chloride either titrated against silver according to the method of Richards and Wells (*Journ. Am. Chem. Soc.*, 1905, xxvii., 459), using a modified nephelometer to determine the end-point, or precipitated as silver chloride and weighed. A new type of apparatus, designed for fractional distillation in a vacuum with the complete exclusion of moisture, was used for the distillation of the vanadyl trichloride and its collection in glass bulbs, and the trichloride was weighed in a manner which obviated the necessity for collecting fragments of broken bulbs.

The results obtained are as follows ($\text{Ag} = 107.88$; $\text{Cl} = 35.457$):—

9 expts.: $\text{VOCl}_3 : 3\text{Ag} = 0.53554 \pm 0.000008$, whence $V = 50.950$.

2 expts.: $\text{VOCl}_3 : 3\text{AgCl} = 0.40307$, whence $V = 50.952$.

For a number of reasons these results may be slightly too low, and the rounded-off value $V = 50.96$ is preferred. This result is in very close agreement with that deduced by McAdam (*Journ. Am. Chem. Soc.*, 1910, xxxii., 1603) from measurements of the ratio $\text{NaVO}_3 : \text{NaCl}$.

DISCUSSION.

In reply to the President, Mr. LITTLE stated that part of the oxide of vanadium which formed the starting material had been formerly used by Sir Henry Roscoe in his researches on vanadium. A small amount of arsenic present in another portion of the oxide was incidentally eliminated when converting the oxide into vanadyl trichloride, but otherwise no initial purification of the oxide was attempted. The vanadyl trichloride, however, was fractionated until a preparation was obtained quite free from phosphorus and arsenic, and having a constant boiling-point (127°). The subsequent fractionation of this product was effected in a vacuum, and no further boiling-point observations were made.

*60. "The Isomerism of the Oximes. Part III. The Hydroxybenzaloximes." By OSCAR LISLE BRADY and FREDERICK PERCY DUNN.

The authors have investigated the hydroxybenzaloximes, but have failed to obtain stereoisomerides or any confirmation of the existence of the supposed isomeric *m*-hydroxybenzaloxime described by Jowett (*Trans.*, 1902, lxxxi., 707). Dollfus (*Ber.*, 1892, xxv., 1924) assumed that in the monoacetyl derivatives of these oximes the

oximino-group was acetylated, but the authors have been able to show that in the case of *p*-hydroxybenzaloxime it is the phenolic hydroxyl that is acetylated, and not the oximino-group, the compound thus being *p*-acetoxybenzaloxime. This and the parent hydroxy-oxime have been proved to possess the *anti*-configuration, and the stereoisomeric *p*-acetoxybenzsynaloxime has been prepared.

In the case of the acetyl derivative of salicylaloxime, however, it has been shown that the oximino-group is acetylated.

DISCUSSION.

Dr. PYMAN pointed out that Dr. Jowett laid no claim to the discovery of a stereoisomeric *m*-hydroxybenzaloxime. The oxime had been prepared from *m*-hydroxybenzaldehyde amongst half-a-dozen other derivatives for the purpose of identification, and the discrepancy of melting-point was noted, but not fully investigated.

In reply to the President, Mr. BRADY stated that it would probably be difficult to obtain stereoisomeric oximes from 4:5-methylene-*o*-tolualdehyde on account of the methyl group being in the ortho-position with respect to the oximino-group; with reference to the methoxybenzaloximes, the two isomeric *p*-methoxybenzaloximes had been obtained, but the ortho-compound existed only in one form; the meta-compound had not been investigated.

In reply to Dr. Pyman, he said that there was no wish on the part of the authors to suggest that Dr. Jowett claimed to have obtained an isomeric *m*-hydroxybenzaloxime; they were, however, of the opinion that it was impossible to obtain a compound melting at 138° by re-crystallising *m*-hydroxybenzaloxime from benzene.

*61. "The Constituents of the Leaves and Stems of *Daviesia latifolia*." By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY.

Daviesia latifolia, R. Br. (Nat. Ord. Leguminosae), is a shrub indigenous to Victoria, Australia, where, on account of the bitter taste of the leaves, it is known as the "Native Hop Bush."

An examination of freshly collected material, consisting of the leaves and stems of the above-mentioned plant, has shown that its bitterness is due to a crystalline benzoyl derivative of a new disaccharide, the latter (*glucoxylose*) yielding on hydrolysis 1 molecule of dextrose and 1 molecule of xylose. The bitter compound possesses the empirical formula $\text{C}_{25}\text{H}_{28}\text{O}_{12} \cdot \text{H}_2\text{O}$, melts at $147\text{--}148^\circ$, and has been designated *dibenzoylglucoxylose*.

Besides a small amount of an aromatic essential oil, the following additional constituents of the plant have been isolated or identified:—Benzoic, salicylic, *p*-coumaric, and fumaric acids, and a mixture of fatty acids, consisting of palmitic, stearic, and linolic acids; a quercetin glucoside, $\text{C}_{27}\text{H}_{30}\text{O}_{16}$, which is probably identical with rutin; myricyl alcohol; hentriacontane; a phytosterol, $\text{C}_{27}\text{H}_{46}\text{O}$; and a sugar which yielded *d*-phenylglucosazone (m. p. 210°). The resinous material, from which some of the above-mentioned substances were obtained, amounted to about 8.6 per cent of the weight of drug employed.

DISCUSSION.

Dr. POWER, in reply to a question by the President, stated that the recent chemical examination of hops had revealed the presence of no substance similar in character to the bitter principle of *Daviesia* leaves. It was also noted that no botanical relationship exists between the leguminous shrub, *Daviesia latifolia*, R. Br., and the common hop plant, *Humulus Lupulus*, L.

In reply to a question by Mr. Baker, it was explained that the new disaccharide, *glucoxylose*, had only been directly isolated in the form of its crystalline benzoyl derivative, *dibenzoylglucoxylose*. The amount of the latter compound present in the leaves appeared to be somewhat less than 1 per cent.

*62. "The Composition of some Mediæval Wax Seals." By JAMES JOHNSTON DOBBIE and JOHN JACOB FOX.

An account was given of the examination of the com-

position of a number of mediæval seals, ranging in date from the thirteenth to the beginning of the sixteenth century.

The seals were found to consist of beeswax alone, or of beeswax mixed with resin in various proportions. The resin could not be identified except in two cases, in which it gave the reactions for colophony.

The red seals were coloured with vermilion, the green with verdigris, the brown and black with verdigris and organic matter.

The beeswax which formed the sole constituent of an impression of the Great Seal of 1350 was practically unaltered in chemical and physical properties, except as regards its power of absorbing iodine, which was slightly less than that which beeswax usually exhibits.

63. "Experiments on the Rate of Nitrification." By RICHARD MOORE BEESLEY.

Solutions of nitrogenous substances were inoculated with a mixed culture of nitrifying and hydrolytic organisms, which were obtained from a secondary contact bed, and the nitrification was allowed to proceed under strictly comparative conditions, with the object of determining the comparative rate of nitrification.

The following substances were employed:—Carbamide, thiocarbamide, uric acid, asparagine, glycine, acetamide, methylamine sulphate, aniline sulphate, ammonium oxalate, and ammonium sulphate. The solutions, with which were incorporated suitable mineral media, were made of such a strength as to contain 100 milligrams of nitrogen per 500 cc.

The course of the nitrification was followed through by means of periodic determinations of the ammoniacal, nitrous, and nitric nitrogen figures. Under these conditions it was found that the various substances nitrified at approximately the same rate, with the exception of thiocarbamide and aniline sulphate, which completely failed to nitrify. Evidence has also been obtained to the effect that in the bacterial oxidation of nitrogen, compounds intermediate between ammonia and nitrous acid are formed.

64. "Studies of the Constitution of Soap Solutions. The Alkalinity and Degree of Hydrolysis of Soap Solutions." By JAMES WILLIAM MCBAIN and HERBERT ERNEST MARTIN.

From electromotive force determinations, the dissociation product of water at 90° is calculated to be 69.7×10^{-14} ; this result is chiefly of interest in discussing the high real temperature-coefficient of the hydrogen electrode, which is ignored by recent convention.

The hydrolysis and true alkalinity of soap solutions has been quantitatively determined for the first time. In concentrated solutions hydrolysis amounts to only a fraction of a per cent, and even in 0.01N sodium or potassium palmitate it only amounts to 6.6 per cent, and thus the high conductivity of soap solutions is definitely shown not to be due to free alkali. The novel suggestion was advanced that it may be due to highly charged aggregates or micelles exhibiting even an equivalent conductivity comparable with that of ordinary ions (see McBain, *Trans. Faraday Soc.*, 1913, ix., 99; *Kolloid. Zeitsch.*, 1913, xii., 256). This suggestion, if confirmed, may apply to such diverse cases as protein salts, dyes, and certain non-aqueous solutions.

In the presence of even one equivalent of free palmitic acid soap solutions are still appreciably alkaline. On the other hand, the alkalinity of solutions containing an excess of alkali is practically that of the added alkali. There is thus no measurable sorption or formation of basic soap in the presence of 0.1N alkali.

Sodium chloride at first decreases, but in larger amounts again increases, the alkalinity of soaps, in accordance with the suggested rule that any influence tending towards coagulation increases the alkalinity of these solutions.

(To be continued).

INSTITUTE OF CHEMISTRY.
Annual General Meeting, March 2, 1914.

Prof. RAPHAEL MELDOLA, President, in the Chair.

THE annual accounts were received on the motion of Mr. A. GORDON SALAMON, the Hon. Treasurer, seconded by Prof. J. MILLAR THOMSON.

The Treasurer's remarks indicated that during the twenty-one years tenancy of its present premises the Institute had been able to make its income suffice for maintenance and steady development, but with the move to the new buildings, which would take place during the present year, the Council would have to look carefully to its resources. Any anxiety on that account would be relieved considerably by the realisation of their hope that the amount of the total expenditure on the new buildings would be subscribed by the end of the year. The response to the appeal to the Buildings Fund was somewhat remarkable in that about £17,000 had been collected at a cost of less than £250. Probably £1000—possibly less—would make the position of the Institute in this respect quite sound, and enable the Architect and Buildings Committee to effect considerable improvements in the finish and equipment of the building.

The Report of the Council having been received and adopted, the meeting proceeded to elect Censors and Auditors.

The PRESIDENT, in the course of his Address to the Fellows and Associates, referred to the progress of the Fund for the new buildings of the Institute, and acknowledged the generous support of many companies, firms, and individuals, other than members, who had contributed. Taking into account the promise of an anonymous benefactor to double every subscription received beyond £12,000 up to the amount of £2500, it was probable that less than £1000 was now required; but if more were received the Buildings Committee could easily invest it in improved and more serviceable finishings. The building had progressed most favourably until the trades dispute, and, as there were signs of approaching settlement, it was hoped that the work would be completed before the autumn.

Referring to the endeavours of the Institute to secure fuller recognition for the profession of chemistry, the President recalled the evidence given by Sir William Tilden and Sir William Ramsay, as representatives of the Institute, before the Royal Commission on the Civil Service. The main portion of their evidence related to the conditions of service of chemists engaged in the Department of the Chief Inspector at Woolwich Arsenal. The Council of the Institute, in the Memorandum submitted to the Royal Commission, stated that the chemical staff in that Department should be controlled by a chemist of the highest efficiency. The rapid development of science in every direction was leading to increased specialisation. The real expert, whose knowledge and experience were of most value to the community, was the highly trained man who had specialised in some particular field. Surely such a man was the most competent to control the work of any public department which was concerned with his own subject. The training and experience which had raised him to his position of efficiency were no less protracted and severe than those required for the attainment of similar status in any other profession. Why, therefore, should there be this tendency to subordinate expert scientific service to non-expert control? The question of national defence was an important one, and the valuation and control of materials required in our arsenals, and the study and application of new discoveries having any bearing upon "the arts of war," were no less matters for chemical control than the conduct of an army in the field would be a matter for control by the General Staff. Yet, while the medical service took army "rank," the chemist, whose services were of equal importance, not only took no

"rank" at all, but was made responsible to superiors having no special knowledge of his subject. This state of affairs, rendering as it did the public service of chemists an unattractive career to the best talent in the profession, was fraught with danger to the future well-being of the country, and was a short-sighted policy which, in time of trouble, might well lead to disaster. It was a matter which could not be lightly dismissed because it affected only a small number of chemists—it was a question of principle of far-reaching consequences, and it was to be hoped that the Royal Commission would give heed to the representations of the Institute.

Another move in this same direction was the re-arrangement of the Chemical Staff of the London County Council which had been carried out since the retirement of Dr. Clowes. Under the new scheme the Chemical Department—as an independent Department—ceased to exist, and the chemical staff was subordinated to the Medical Officer of Health. This, again, appeared to be a distinctly retrograde step, and one which the Institute could not but deplore. The matter had been represented to the Chairman of the County Council, Mr. Cyril Cobb, and he had made it perfectly clear that in this re-arrangement there had been no intentional slur cast upon the status of the chemical staff; but it was a dangerous precedent, and one which the Institute regarded with apprehension for several reasons. There was the impression left on the public mind that the services of the chemist were of less importance than formerly; whereas, in fact, as time went on they were certain to become more and more important. Further, there was conveyed the idea that the status of the professional chemist was an inferior one—in other words, that his profession was to be degraded in rank with corresponding exaltation of a kindred profession, a principle to which the Institute could not give its sanction.

The Council had also dealt with the conditions of appointments of Public Analysts, on which subject they had prepared a statement which had been published in the *Proceedings*, and would be issued to members of many local authorities. The Council hoped that, by this publication, the authorities might realise and appreciate more fully than they appeared to have done in the past the nature and responsibilities of these public officers.

In other branches of the profession, particularly in its applications to industry, the prospect for young chemists was improving. Not only was there little difficulty in placing Associates in appointments, but they were offered higher commencing salaries than formerly, and, although the cost of living had greatly increased, they were generally able to secure a "living wage" in most branches of the profession at the outset of their careers, which was much less frequently the case a few years ago.

Prof. Meldola then dealt at considerable length with the Report of the Conference of Professors of Chemistry, held under the auspices of the Institute in October last, which was attended by professors from practically all the principal educational centres of the country, the Institute thus providing an area for the free discussion of the broad question of the education of professional chemists. The Report of this important meeting was under the consideration of a Special Committee composed of representatives of every department of the profession—professors and teachers, private consultants, practitioners, and those who are accustomed to the scientific control of industries. Their task would be one of no little magnitude, and would probably effect considerable re-casting of the Regulations of the Institute in the light of modern educational development. Whatever scheme might eventually be adopted it was certain that the Council would safeguard the status of the existing members. Professors and teachers would gladly welcome the support which the Institute might lend to their endeavours to raise the educational level to the required standard, while senates, councils, and governing bodies could not afford, on public grounds, to set aside curricula of studies, or to ignore a standard regarded as essential for efficient training for the chemical profession

by a body fully representative of that profession. It was in this way that the influence of the Institute in the educational world might, through a revision of the existing Regulations, be exalted into a still greater power, making for the highest efficiency of the chemist of the future.

Sir WILLIAM RAMSAY, in proposing a vote of thanks to the President for his Address, endorsed the views which had been expressed with reference to placing men having no technical knowledge in the control of experts, and remarked on the absurdity of requiring them to sign reports only fully understood by the specialist. He also bore testimony to the fact that the Institute was of the greatest possible service not only to young professional chemists in securing them appointments, but also to manufacturers and authorities who required the services of such chemists. He hoped that the Conference of Professors of Chemistry would result in a working arrangement being devised to attract all properly trained and competent young chemists to the ranks of the Institute.

The vote was seconded by Mr. JOHN SPILLER, and carried unanimously.

The PRESIDENT, having replied, submitted the report of the Scrutineers.

The following were elected Censors:—Dr. George Beilby, F.R.S., Prof. Percy F. Frankland, F.R.S., Mr. David Howard, and Dr. George McGowan.

The Officers and Council for the ensuing year were elected as follows:—

President—Raphael Meldola, D.Sc., LL.D., F.R.S.
Vice-Presidents—George Thomas Beilby, LL.D., F.R.S.; Edward John Bevan; James Johnston Dobbie, LL.D., D.Sc., F.R.S.; Sir Alexander Pedler, C.I.E., F.R.S.; Sir Boverton Redwood, Bart., D.Sc.; Edward William Voelcker, A.R.S.M.

Hon. Treasurer—Alfred Gordon Salamon, A.R.S.M.
Members of Council—Leonard Archbutt; Robert Frederick Blake; Arthur George Bloxam; William Thomas Burgess; Cecil Howard Cribb, B.Sc.; Charles Frederick Cross, B.Sc.; Martin Onslow Forster, D.Sc., F.R.S.; Gilbert John Fowler, D.Sc.; Sir Richard Garton; Arthur Harden, D.Sc., Ph.D., F.R.S.; Otto Hehner; Charles Alexander Hill, B.Sc.; Edward Hinks, B.Sc.; William Richard Eaton Hodgkinson, Ph.D.; Alfred Henry Knight; Henry Rondel Le Sueur, D.Sc.; William Macnab; Gordon Wickham Monier-Williams, M.A., Ph.D.; Francis Richard O'Shaughnessy, A.R.C.S.; William Henry Perkin, LL.D., Ph.D., F.R.S.; Sylvester Oliffe Richmond; Clarence Arthur Seyler, B.Sc.; Thomas Stenhouse, jun., B.Sc., A.R.S.M.; Frederick Wallis Stoddart; Oliver Trigger; William Henry Willcox, M.D., B.Sc.; James Woodward, B.A., B.Sc.

Mr. W. J. A. Butterfield, Dr. Percy E. Spielmann, and Mr. Herbert F. Stephenson were elected Honorary Auditors.

With a vote of thanks to the retiring Officers and Members of Council the meeting terminated.

Institute of Chemistry.—Mr. William Macnab, F.I.C., will deliver the second lecture on "Explosives," on Thursday, March 26, 1914, at 8 p.m., at King's College, Strand, London, W.C., Prof. R. Meldola, D.Sc., F.R.S., President, in the Chair. *Syllabus*.—General description of Rules and Regulations prescribed by the Explosive Department of the Home Office for the construction and working of explosive factories. Description of processes and plant used in the manufacture of the principal explosives. "Permitted" explosives for use in fiery coal-mines, and the Home Office Test which they have to pass. Military propellants and the conditions which they have to fulfil. Recent filling material for shells. Sporting powders: general characteristics. Novel application of explosives. Scope of the chemist's work in connection with explosives.

NOTICES OF BOOKS.

Studies in Water Supply. By A. C. HOUSTON, D.Sc., M.B., C.M. London: Macmillan and Co., Ltd. 1913.

THIS monograph is practically a summary of papers and articles published by the author, embodying the results of his personal experiences and giving accounts of his investigations. Local authorities as well as those who are engaged in water analysis will find it very convenient to be able to procure a collection of all the author's valuable work carried out while he has been Director of Water Examination to the Metropolitan Water Board. While the book is essentially an account of the author's own experiences other publications are not altogether unnoticed, and they are always very impartially criticised. Many tables of results and graphical representations are given relating to bacteriological and chemical tests, and processes of purification and sterilisation are clearly described. The question of the connection between the purity of the water supply and the prevalence of disease is lucidly treated, and a valuable feature of the book is the detailed description of the routine methods of bacteriological work. Methods of collecting and labelling samples, registering results, and decimally diluting samples are first treated, and a chapter is devoted to the detailed description of the exact method followed in the examination of a sample of raw river water. Full accounts are included of each day's work, and the composition of the culture media used for the different tests is also given.

Les Catalyseurs Biochimiques dans la Vie et l'Industrie. ("Biochemical Catalysts in Life and in the Industries"). By JEAN EFFRONT. Paris: H. Dunod and E. Pinat. 1914.

THIS treatise on the proteolytic enzymes gives a detailed account of the work which has been done on the catalysts of nitrogenous matter. The preparation and properties of the individual enzymes, pepsin, trypsin, amylases, and the study of the products resulting from them are carefully described. Most of the numerical data given and the methods of analysis have been verified and tested by the author, who reveals in the text an extensive knowledge of his subject in all its branches. The book contains an important chapter on the coagulation of the blood, in which recent work is well summarised and critically examined. The applications of diastatic reactions in the industries are also treated, and the important parts played by the enzymes in therapeutics, brewing, tanning, &c., are admirably described, while the methods of analysis of the products of proteolysis which may be employed in the study of medical problems such as the process of digestion are also included.

Annuaire pour l'An 1914. Paris: Gauthier-Villars.

THE physical and chemical tables given in this annual published by the Bureau des Longitudes have been revised, and some interesting new articles have been added. These include one by M. Bigourdain on "Le jour et ses divisions," which gives a short account of the history of primitive methods of dividing the day, and also discusses the question of the unification of the astronomical and civil day and methods of transmitting the time. A second short article by M. Ph. Hatt deals with the deformation of images by telescopes.

Taschenbuch für die Anorganisch-Chemische Grossindustrie. ("Pocket-book for the Inorganic-chemical Major Industries"). By Prof. Dr. G. LUNGE and Dr. E. BERL. Fifth Edition. Berlin: Julius Springer. 1914.

THE fifth edition of this useful pocket-book is characterised by the same excellent features which deservedly won success for the earlier issues. The statistics and data have in all

cases been accurately brought down to date, and many new tables of constants have been added, a great number being taken from Landolt's "Physikalisch-chemische Tabellen." New methods of analysis are also described, the experimental directions being very fully given, and every care has been taken to provide clear descriptions of reliable methods only. All numerical results have been recalculated on the values given by the International Atomic Weight Commission for the year 1913 on the basis $O = 16$.

CORRESPONDENCE.

ATOMIC WEIGHTS.

To the Editor of the Chemical News.

SIR,—If a Rydberg series (CHEMICAL NEWS, xcix., 149) be arranged for all the elements, consisting of odd and even whole numbers progressively differing by four units (= the atomic weight of a helium atom), it can be shown that the decimal fractions can be accounted for by considering the elements as mixtures of whole number components selected therefrom, thus:—

Copper.	Silver.	Gold.
$63 \times 7 = 441$	$107 \times 7 = 749$	$196 \times 7 = 1372$
$67 \times 1 = 67$	$111 \times 2 = 222$	$200 \times 3 = 600$
8)508	9)971	10)1972
63.5	107.88	197.2

I believe that Prof. Soddy was the first to make an observation based upon radio-active experiments that the common elements might be mixtures, although Sir William Crookes in 1887 suggested that the atomic weights might be mean values.—I am, &c.,

F. H. LORING.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 4, January 26, 1914.

Chlorides of Iridium.—Marcel Delépine.—The author prepared a specimen of the yellow powder obtained by the action of sulphuric acid on the chloroiridites and then raised it to temperatures of 200° , 300° , 400° , 450° , and 500° in a current of dry hydrochloric acid gas for at least an hour. Progressive variations of composition then took place, and the composition gradually approximated to the formula IrCl_3 . At 600° decomposition began with liberation of chlorine and formation of a mixture of reduced metal and anhydrous iridium chloride. Apparently the substances obtained, even at 500° , are not the anhydrous chloride but substances of formula $\text{IrCl}_3 \cdot m\text{HCl} \cdot n\text{H}_2\text{O}$, where m and n are small fractions. The chlorides obtained up to 500° are distinguished from the anhydrous chlorides by their hygroscopicity and their solubility. The aqueous solutions of the chlorides prepared at 400° , 450° , and 500° can be concentrated. If the residue is redissolved and again evaporated a black mass is obtained which, after being dried at 100° , has very nearly the composition $\text{IrCl}_3 \cdot 1.5\text{H}_2\text{O}$.

Vol. clviii., No. 5, February 2, 1914.

Alkylation of the Cyclopentanones and Rupture of the Cyclic Chain of Tetraalkyl Derivatives by Sodamide.—A. Haller and R. Cornubert.— α -Methylcyclopentanone can be prepared by methylating ethylcyclopentanone carbonate and decomposing the substituted ether by means of concentrated hydrochloric acid. The di-, tri-, and tetra-compounds can be prepared by successive methylations. The boiling-points of these derivatives increase regularly with the number of methyl radicles, while the reverse is the case for the densities and indices of refraction. α -Methylcyclopentanone fixes only two allyl groups. When sodamide acts on tetramethylcyclopentanone the amide of 2.2.5-trimethylcaproic acid is obtained.

Influence of Shaking upon the Solution of Copper in Nitric Acid.—Maurice Drapier.—When copper is dissolved in nitric acid solution no longer occurs, or else progresses slowly, when the liquid is shaken. It might be supposed that this is due to the fact that the heat of solution produces a local elevation of temperature which shaking renders impossible. Experiments, however, show that this explanation is not correct. If a stick of copper is made to rotate on its axis at different rates in solutions of nitric acid it is found that the quantity of copper dissolved in a given time first slowly diminishes as the rate of rotation increases. Above this critical rate the velocity of solution rapidly decreases and finally vanishes. The critical rate increases with the concentration of the acid. It is possible that the solution of copper in nitric acid is an autocatalytic reaction, and the agitation of the solution by diluting the products of reduction of the acid puts off the moment at which their concentration reaches the stage at which the reaction is appreciably catalysed.

Bulletin de la Société Chimique de France.

Vol. xv.-xvi., No. 2, 1914.

Reaction of Succinic and Malic Acids.—W. Giesner de Coninck.—A concentrated aqueous solution of succinic acid is added to some grms. of calcium salicylate in a little cold water, and the whole is gently heated. A pale pink coloration soon appears. This coloration is very stable, and in the author's experiments it persisted for eight days, even when the flask was exposed to sunlight for some hours each day. With malic acid a similar coloration is obtained, but it is not so stable, and if the liquid is gently boiled for fifteen to twenty minutes the colour fades. After some hours the liquid becomes a light yellowish brown. This reaction can be employed to verify the presence of succinic or malic acids in a liquid.

MISCELLANEOUS.

Royal Institution.—On Tuesday, March 24, at 3 o'clock, Mr. A. H. Smith, Keeper of Greek and Roman Antiquities in the British Museum, begins a Course of two lectures at the Royal Institution on "Landscape and Natural Objects in Classical Art"; and on Thursday, March 26, Dr. C. W. Saleeby delivers the first of two lectures on "The Progress of Eugenics"—(1) The First Decade 1904—1914; (2) Eugenics of To-day, its Counterfeits, Powers, and Problems." The Friday Evening Discourse on March 27 will be delivered by Prof. J. A. Fleming on "Improvements in Long Distance Telephony"; and on April 3, by Prof. Sir J. J. Thomson on "Further Researches on Positive Rays."

Faraday Society.—A General Discussion on "Optical Rotatory Power" will take place on Friday, March 27 next, in the rooms of the Chemical Society, Burlington House, London, W. The meeting will be open to Fellows of the

Chemical Society and Members of the Physical Society of London. Others interested in the subject and desirous of being present should apply to the Secretary of the Faraday Society. The following provisional programme has been arranged:—

5.0. Prof. H. E. Armstrong, F.R.S., will preside at the Afternoon Session and deliver an Introductory Address. Prof. Dr. Hans Rupe (Basle) will read a paper on "Some Contributions to the Knowledge of the Influence of certain Groups on Rotatory Power." Prof. Dr. H. Grossmann (Berlin) will read a paper on "New Studies in the Rotatory Dispersion of Tartaric Acid and Malic Acid." Dr. E. Darmon (Paris) will read a paper on "The Existence of Racemic Tartaric Acid in Solution." Prof. Dr. Leo Tschugaeff (St. Petersburg) will communicate a paper on "Anomalous Rotatory Dispersion." Dr. T. M. Lowry and Mr. T. W. Dickson will read a paper on "Normal and Anomalous Rotatory Dispersion."

6.30—8. The meeting will adjourn for Dinner at the Trocadero Restaurant.

8.15—10. Prof. Percy F. Frankland will preside at the Evening Session. Dr. T. M. Lowry and Mr. H. H. Abram will exhibit some apparatus for measuring Rotatory Dispersion, and will read a paper on "An Enclosed Cadmium Arc for Use with Polarimeter." Dr. R. H. Pickard and Mr. J. Kenyon will read a paper on "The Relations between the Rotatory Powers of the Members of Homologous Series." Dr. T. S. Patterson will read a paper on "The General Behaviour of Optically Active Compounds as regards the Dependence of Rotation on Temperature, Dilution, Nature of Solvent, and Wave-length of Light." The meeting will then be open for general discussion.

MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Royal Society of Arts, 8. (Howard Lecture). "Surface Combustion," by Prof. W. A. Bone, F.R.S.

TUESDAY, 24th.—Royal Institution, 3. "Landscape and Natural Objects in Classical Art," by A. H. Smith, M.A.

WEDNESDAY, 25th.—Royal Society of Arts, 4.30. "Fashion in Art," by Sir Charles Waldstein, Ph.D.

THURSDAY, 26th.—Royal Institution, 3. "The Progress of Modern Eugenics," by C. W. Saleeby, M.D., &c.

Royal Society. "Nature of the Tubes in Marsupial

Enamel and its bearing upon Enamel Develop-

ment," by J. H. Mumery. "Oxidation of Thio-

sulphate by certain Bacteria in Pure Culture," by

W. T. Lockett. "Production of Anthocyanins

and Anthocyanidins," by A. E. Everest. "Vari-

ations in the Growth of Adult Mammalian Tissue

in Autogenous and Homogeneous Plasma," by

A. J. Walton. "Decomposition of Formates by

B. coli communis" and "Enzymes which are con-

cerned in the Decomposition of Glucose and

Mannitol by *B. coli communis*," by E. C. Grey.

"Description of a Strain of *Trypanosoma Brucei*

from Zululand—Part I., Morphology; Part II.,

Susceptibility of Animals," by Surg.-Gen. Sir D.

Bruce, Major A. E. Hamerton, Capt. D. P.

Watson, and Lady Bruce.

Chemical, 4.30. (Annual General Meeting).

President's Address, "Recent Researches on

Tautomerism."

FRIDAY, 27th.—Royal Institution, 9. "Improvements in Long Dis-

tance Telephony," by Prof. J. A. Fleming, F.R.S.

Faraday Society, 5. General Discussion on "Optical

Rotatory Power."

Physical, 5. "New Type of Thermogalvanometer,"

by F. W. Jordan. "Instrument for Recording Pres-

sure Variations due to Explosions in Tubes," by

J. D. Morgan. "Direct Measurement of the

Napierian Base," by R. Appleyard. "Experiment

with an Incandescent Lamp," by C. W. S. Crawley.

SATURDAY, 28th.—Royal Institution, 3. "Recent Discoveries in

Physical Science," by Prof. Sir J. J. Thomson,

O.M., F.R.S.

ERRATA.—P. 117, col. 2. At bottom read:—"It is true that $\frac{dP}{dx}$, $\frac{dp}{dx}$, and $\frac{dp_2}{dx}$ are all zero. It is, however, not necessary

that $\frac{dP}{dy}$ shall also be zero, and hence $y=x$. $\frac{dP}{dy}$ does not change signs," &c. At top of p. 118, the vinculus should only include $y-x$, and not $y-xP$.

THE CHEMICAL NEWS.

VOL. CIX., No. 2835.

NOTES ON PLANT CHEMISTRY.

By P. Q. KEEGAN, LL.D.

Incidents of Analysis.

THE utility of what is known as Millon's reagent in plant analysis is occasionally very evident. The proper way to prepare it for this purpose is as follows:—Place some red HgO at the bottom of a long narrow test-tube, add a few drops of water to moisten, and then some glacial acetic acid, warm, not boil, till the oxide is dissolved, and then immediately pour the solution into a bottle, which stopper well and keep in the dark. After a time crystals form in the liquid, but never mind; when using it shake well up, and pour at once two or three drops into the solution to be tested, add one or two drops dilute solution of KNO₃, and slowly warm, when the coloration will appear. In this way we obtain in most cases a coloured solution and not a precipitate, which latter frequently occurs when the reagent is prepared by dissolving precipitated HgO in dilute acetic acid.

Occasionally it is very difficult to obtain well formed crystals of oxalate of calcium from leaves under analysis in the ordinary course, *i.e.*, by the last extraction by dilute HCl. In this case wash the final residue on the filter with water, and dry it or leave it to dry in the air, then powder a portion of it very fine, pour over it placed in a bottle strong HCl, diluted with equal volume of water, and cooled; leave for five days, filter off the solution, and add sufficient solid acetate of soda and a little acetic acid to precipitate the oxalate; stand one day, decant, wash the crystals, and examine under the microscope, when an extraordinary success will be reported. Two particularly bad cases, *viz.*, the leaves of beech and of water-lily, yielded by this treatment magnificently clean and beautifully formed crystals of oxalate, wherein the crossed markings and colour contrasts were clearly visible by the light of an ordinary condenser.

A recent statement by Lloyd, that "in certain cells of the pericarp of fruits the tannin exists in a sort of solid solution with a pectose which absorbs it, and hence it cannot be extracted," is hardly referable to fruits only. According to my own experience it is very difficult and sometimes impossible to extract all the tannic matter from either leaves or barks. In the case of very mucilaginous leaves or roots alcohol frequently extracts no tannin at all, *e.g.*, species of buttercup, comfrey root, &c., and it requires two or three relays of boiling water and concentration of the solutions before a sufficient amount is extracted, even for purposes of mere qualitative recognition. In some cases the second aqueous extract contains probably twice as much tannin as the first, and it must needs be that these facts were unknown to some of the old analysts, otherwise their reports would in many important instances have been fuller than they are. Owing to the difficulties of the extraction of tannin from the material and of its complete purification from tannoid, &c., any attempt to determine its quantity accurately is in most cases hopeless. Then, again, there is the question of the instability, impurity, &c., of gallotannin especially. The decomposition of a catechol tannin might take place in two ways, *viz.*, by a kind of absorption of it by a pectose followed by the production of a brown "humins" quite refractory to fused

alkalis, or also of a partial transformation of its phenolic groups, or rather of an addition to their number. This is evidently the case with the bark and leaves of oak, beech, and Spanish chestnut. All these tannins give the HCl vanillin reaction decisively, but do not give the iodine test for gallotannin quite satisfactorily; with Millon's reagent they sometimes turn blue, but at other times there is a green precipitate only, or a deep red and green dichroic solution. The tannin of certain Rosaceæ and of Saxifragaceæ behave in a very similar way, but in my opinion there is nothing very serious in these facts; *i.e.*, there is no great magical alchemy in the partial transformation of a catechol tannin into gallotannin, while the phloroglucol group thereof remains intact. In fact, there are cases, *e.g.*, that of *Ribes sanguinea*, known as the flowering currant, where the whole of the catechol group has apparently been destroyed, leaving nothing but a voluminous red phlobaphene and a quantity of phloroglucol; so that you have the rather startling phenomenon of an apparently catechol tannin yielding no protocathechuic acid on fusion with potass. A study of the vigorous physiological processes, in many cases assuming the character of pathological ones, going on in the barks of trees and shrubs, indicates that intense chemical changes take place also in connection therewith. The normal progress of the thickening growth of the axis of the tree reacts powerfully on the tissues of the cortex, inducing sclerosis or destruction of its external tissues, hypertrophy, flattening of the cells, formation of periderm and rhytidome, &c. In all these cases there is an intense absorption of oxygen, *i.e.*, there is a co-operation of the chemical energies immanent in the system which is constituted by the plant itself in conjunction with the oxygen of the air. The oxidation varies considerably in intensity according to the anatomy or histology or plicancy of the various organs, and this fact would account for the varying amount of gallotannin, or perhaps gallic acid found in bark, wood, or fruits of certain species of oak, beech, Spanish chestnut, and other Cupuliferae.

In the course of studies on anthocyan it was found necessary to trace the connection between certain specially vivid or beautiful colours shown by certain flowers and the decomposition products of the tannins which the plants bearing these flowers produce. In other words, it was sought to prove what some enquirers had denied, *viz.*, that a chromogen of anthocyan does actually exist. And as gardeners had apparently cultivated a blue variety of the Chinese primrose, a few species of the order Primulaceæ were examined. Both the young and old leaves of the common primrose were found to contain tannoid only, though there seemed to be a little tannin in the leaves got in June on the outskirts of a wood in a damp rocky locality; the flower stock and flowers, however, contained considerably more tannin which was phlobaphenic, gave the vanillin HCl reaction decisively, and precipitated gelatin, the precipitate being tinged deep blue by solution of iron alum. The leaves of the yellow loosestrife were found to contain tannoid and a tannin reacting precisely as that of the primrose, and all the more distinctly inasmuch as its quantity was much greater. Another plant, the sea pink, belonging to an allied order, was analysed; it contained what may be called a tannide, yielding reactions similar to the above, except that with vanadate of ammonium a blue colour, with peracetate of iron a blue-violet precipitate, and with nitrate of silver a beautiful red coloration were produced; on potass-fusion it yielded phloroglucol only, whereas in the other two cases protocathechuic acid was also obtained. All three were phlobaphenic, and all on careful warming with dilute HCl yielded an extremely beautiful red solution vividly recalling as to tint and otherwise the pigment which decorates the petals of the well-known winter primula of the greenhouse. On the strength of this investigation it was concluded that there is a clear genetic connection between tannin and pigment and that the natural species (*carniola*, *frondosa*, *sapphirina*) or the cultivated varieties or hybrids (*sinensis*, &c.), of

primula are not true blues, but rather what a horticultural writer describes as a "wishy-washy lilac-cum-lavender-cum-purple" affair.

It is not surprising that the HCl-vanillin reaction for phloroglucol should have attained great prominence. As a macro reagent on the tissues it is worthless. The correct coloration that should ensue on its application is a rather dull vermilion-red, and not a violet or purple-red. Waage's famous histological researches (1890) over the presence of phloroglucol in plants are surprisingly accurate in the main, but it is doubtful if there exists, as he states, any phloroglucol tannin in cornus, crocus, cœnothra, coffee, peucedanum, scorzonera, clematis, strophantus, lilac, viburnum, symphoricarpos (all except the first three contain caffetannin or caffeic acid). He finds no phloroglucol in the examined Rutaceæ, Caryophyllaceæ, Cruciferae, or Papaveraceæ; but he rather overlooks the Primulaceæ and Plumbaginæ, which contain several species producing splendid tannins or tannides that yield the HCl-vanillin reaction decisively. It is necessary to evaporate to dryness a little of the purified alcoholic or aqueous extract of the leaves, &c., add a little vanillin and a drop or two of HCl, when the dull vermilion-red will immediately appear. Extracts of plants which contain pure gallotannin, caffetannin, or tannoid only do not yield the reaction, and it is most advisable to purify by alcohol all aqueous solutions or extracts containing gallotannin or gallic acid before applying the test, otherwise a dirty violet colour, due apparently to "humins" or to a high anhydride, sometimes appears, which may prove seriously misleading.

The paper by Prof. A. G. Perkin on "Quercetagenin," published in *Trans. Chem. Soc.* (1913), is, from a purely scientific point of view, of the utmost value and importance. Therein for the first time, so far as I know, it is recognised by a professed investigator that a certain flavonol derivative (tannoid) contains a nucleus with a quinol grouping in place of the ordinary phloroglucol nucleus. I might here, however, take the liberty of stating that on four different occasions in my published papers I asserted the existence of a quinol nucleus in the tannoids of certain plants belonging to the Compositæ and Labiata orders. I considered that there must be present somewhere a tannoid corresponding to caffetannin, and it would seem now to be settled that what bears the name quercetagenin represents that required substance. What is remarkable is that it has apparently never before been sought for and distinguished specifically by those whose means and instruments of research are superior to mine.

Some years ago the botanical world was startled when some enterprising Scot had discovered a blue poppy on the Himalayan mountains. Since that period several other blue poppies have been discovered, and a large area of western China and thereabouts has been christened "the land of the blue poppy." All these are of the genus *Meconopsis*, and, in fact, *M. speciosa*, of a glorious Cambridge blue, is reckoned one of the most beautiful flowers in existence. Fortunately there is one native species, the Welsh poppy (*M. cambrica*) of this genus in Eng and, and as it is found in this valley, I secured a few leaves thereof, and analysed them with special reference to the existence therein of a chromogen precursive of a true blue pigment. The leaves were very mucilaginous, and hence on boiling them with alcohol no tannic matter was extracted; the residue, however, was dried and boiled twice with water, and both extracts, on purification from mucilage, &c., gave decisive reactions of caffetannin. Thus it would appear that this blue poppy sensation was no sham, and in accordance with the results of my previous researches the petals of this genus of plants were adjudged competent to evolve a pure blue pigment. The leaves contained much nitrate, and also much oxalate of calcium in large fine crystals. Their ash yielded 43.6 per cent soluble salts, 3.3 silica, 26.3 CaO, 4.2 P₂O₅, 6.6 Cl, 12 SO₃, and only a little iron and manganese.

Patterdale, Westmorland.

NATIONALISATION OF SOURCES OF RADIUM IN UNITED STATES.*

REPORT OF COMMITTEE ON MINES AND MINING.

(Concluded from p. 138).

Foreign Demand.

As already stated, by far the larger part of the radium ore so far produced in the United States has been shipped abroad, and, even worse than this, that portion of the radium which is being extracted in America has also been largely contracted for foreign delivery. This has opened up to foreign medicine and science opportunities for the investigation and treatment of malignant diseases that have been denied to the American people, except by purchase of manufactured radium compounds at almost prohibitive prices. To-day there is probably less than 2 grms. of radium salts in the possession of physicians in America, which, considering the almost miraculous cures of cancer shown to the Committee by reputable surgeons through the means of plaster casts and photographs, is appalling. In Europe a very different condition exists. During the past year extensive appropriations have been made there for the purchase of radium and mesothorium, showing the great demand that has arisen for these materials in the treatment of cancer. Some of these purchases have been made by Government appropriation and some by municipal or other public subscription. The Austrian Government has expended 600,000 dols. for the purchase of deposits of radium-bearing ores, and has made subsequent provision for the mining of these ores and the extraction of the radium. Prussia has appropriated 370,000 marks for the purchase of 1 gm. of radium bromide.

Radium in Cancer Work.

Three leading surgeons of America who have themselves had extensive experience in the application of radium in the treatment of malignant diseases, viz., Dr. Howard A. Kelly, of Baltimore; Dr. Robert Abbe, of New York; and Dr. Curtis F. Burnam, of Baltimore, have appeared before the Committee, and have shown casts and photographs of cancer cures actually brought about in their practice, which appear to the Committee to be in themselves more than sufficient argument for the proposed legislation. These three surgeons and Dr. H. R. Gaylord, Director of the New York State Cancer Laboratory, have favoured the general principles outlined in this Bill, have expressed their inability to procure more radium for their own practice, and have emphasised their great need and desire for more of this material to be used in treating the sufferers of the most malignant of diseases. Large sums are appropriated each year for the treatment of the diseases of animals, for the destruction of pests, and various sums for other important objects for the benefit of the people. It has been demonstrated beyond a doubt that this remedy is a cure for external malignant growths.

Hoffmann, the statistician, estimates that each year 75,000 people die from these growths known as malignant. If this remedy will cure 20 per cent we have saved 15,000 lives each year. The cause of cancer is to-day unknown, so physicians must apply themselves to the cure until someone discovers the cause, so that it will be known how to prevent this disease.

If the Government does not secure these ores bearing radium it is quite likely that large quantities will be shipped out of the country, and what is extracted in America will fall into the hands of those who will have a monopoly, and the price will be so high that it will be out of the reach of poor people. As it has been well said, "cancer is the poor man's disease, and radium is the rich man's remedy."

* Slightly abridged from Report No. 214 of the House of Representatives, 63rd Congress, and Session.

If this Bill becomes a law it may be hoped that in time the Government will control this remedy so that it may be placed in all parts of the country, readily accessible to all those who may be so unfortunate as to require its use, and may secure the treatment without having to pay an exorbitant price. It is certainly better for the Government to have the monopoly than the private individual in so important a curative agent for disease, with which no one can be assured they will never be afflicted.

It is now estimated that the hospitals belonging to the United States ought to have at least 25 grms., and at the present price it would cost 120,000 dols. per grm., which would mean the expenditure of a large sum to secure the amount thought necessary. It has been shown that foreign buyers have been securing all the ore they could and shipping it to their own country and extracting the metal, and then the Americans have been obliged to buy the radium from them. It is important that the American people should have the control of the remedy which lies in the public lands which the Government now owns.

Radium Institutes.

Several radium institutes have been founded throughout the world for studying the application of radium to science and to disease. Some of these are private and some are public. Prominent among them may be mentioned the Radium Institute of Austria, founded under a donation given by Dr. Kuppelweiser to the Academy of Science of Austria, which now has one of the largest supplies of pure radium salts used chiefly in scientific investigations. In Paris a new radium institute under the direction of the Sorbonne has been built by this University near the Pantheon. In England the London Radium Institute was founded by Sir Ernest Cassel and Viscount Iveagh, who gave a large sum for its endowment. This Institute is making a special study of the application of radium to disease. In America the National Radium Institute has recently been founded by Dr. Howard A. Kelly, of Baltimore, and Dr. James Douglas, of New York.

Difficulty of Securing Radium on any other Basis than Government Operation.

At present, on account of the tremendous demand for the material abroad, there is no means of keeping radium ores or radium in America, except by overbidding the excessive price now being offered for them in European markets; and this means that the American people must buy back from foreign countries at speculative and exorbitant prices the very radium which was their own, and which their Government has allowed to become subject to foreign exploitation. It has already been shown that foreign Governments and municipalities are prepared to pay prices for radium far in excess of the cost of production and manufacture, and they have already obtained more than half of the available ores produced in the United States. It was in France, Germany, and Austria that the value of radium was first appreciated. Here a demand for it was first established and processes for extracting it from these ores were developed. Meanwhile the American Government has been giving away its deposits of radium-bearing ores, which even though limited are the most extensive known, and allowing them to pass into the ownership of a foreign corporation, a few American companies acting as shipping agents for other foreign corporations or to an American company which sells its radium largely to foreign purchasers. The high price of radium salts—by far the larger part of this price representing a profit to the manufacturer—is taking radium out of the country, and even if it stays in the country the present price makes its use so expensive that the material can hardly be expected to be available to people of small means, except in so-called charity cases. Accordingly it seems extremely important that the United States Government shall make such provision as shall be necessary to obtain supplies of

radium requisite to meet the more urgent needs of the American people. The responsibility for this neglect and delay in development in the United States rests with the scientific men in the universities, with the Government service, and with Congress itself. The legislation now proposed is intended to remedy this situation.

Appropriations.

The Committee after due deliberation has asked for an appropriation of 150,000 dols. for the erection and general equipment of a suitable building or buildings for radium extraction and other work of the Bureau of Mines in the metal-mining States, and the further sum of 300,000 dols. for the necessary expenses connected with the purchase and treatment of radium-bearing ores and the extraction of radium therefrom during the fiscal year ending June 30, 1915. The Committee believes that these amounts are less than should be allotted to this important work, but believes also that they will be sufficient for the erection and equipment of the extraction plant and the purchase of such ores as can be procured in the fiscal year 1915, and will enable the department to get the work well under way. It is expected that the buildings to be erected under this appropriation of 150,000 dols. will be inexpensive structures that will be located at points best adapted to the success of this radium work. The larger part of this appropriation is for the engineering equipment necessary in the concentration and treatment of the ores and the extraction of the radium. The other appropriation (300,000 dols.) will be used for the purchase of ores (covering the cost of mining) and for the chemical equipment and supplies and general operating expenses. It is expected further that if the necessary supply of ore be obtained the commercial value of the radium extracted under this appropriation will be far in excess of the total amount of the appropriation authorised in this Bill.

The Committee believes that the welfare of the American people and especially the alleviation of those suffering from that terrible malignant disease, cancer, demand that this Bill be passed, and that this important work be initiated without undue delay.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

A RADIUM PARATONNERRE.

Whereas the pointed lightning-rod has no preventive action, and only a limited local action, M. Szilard has discovered that by supplying it with a screen furnished with radium (1 to 2 milligrams suffice), it is possible to give it most interesting qualities. The radium renders the layers of air (even those far removed from the point) several millions of times more conductive than is ordinary, and this effect produces an exchange of electricity between the different superposed atmospheric layers. Simultaneously an outlet of electricity is produced between the atmosphere and the Earth, and that happens, not only in a fashion limited to the point, but by a constant uninterrupted current passing through a layer of air with a radius of several dozens of metres, which the progressive conductivity of the air towards the point concentrates towards its direction. And this conductivity is so much the greater in proportion to the strength of the electrification of the atmosphere. But if, in spite of all preventive action great discharges are produced, they undergo at the same time the effect of the conductivity of the air which will transport them from a pretty considerable distance to the paratonnerre, and the priming effect that the radioactive rays exercise on the sparks in making them flash out in a primitive state of development. We have thus a lightning-rod that is preventive against all the electric manifestations of the atmosphere and a paratonnerre with

a large radius of action. The paratonnerre of this principle realised by M. Szilard has enabled him to verify and even measure these actions. The results have proved superior, from all points of view, to those obtained by ordinary paratonnerres. It is curious to remark that a Geissler tube joined to the new paratonnerre is lighted even in calm weather. These encouraging experiments merit to be continued in a large measure.

NEW CULTURES OF AN EDIBLE MUSHROOM.

For the last twelve years Prof. Louis Matruchoth has been making lengthy experiments with a view of seeking out the influence of the conditions of environment on a new cultivable species of edible mushrooms, called the "blue foot," or *Tricholoma nudum*. The experimentation on these fleshy mushrooms is the more difficult seeing that their evolution is exceedingly slow. The cultures of blue-foot have been established on ricks or heaps of beech leaves in the cellars of the Paris Observatory; that is to say, in complete obscurity and in a temperature of 11°. The species cultivated by the method of M. Matruchoth becomes modified. It produces in all seasons instead of only in the autumn. In a state of nature the blue-foot, an autumnal species, is rarely to be seen excepting in the period from October to December. In his trials of culture in collaboration with M. Costantin, of the Natural History Museum, M. Matruchoth has gathered mushrooms at periods from January to July. With the new cultures, in the cellars of the Observatory, there has not been a single month in the year when he has not been able to gather the blue-foot. The proof is then made, that this edible and much sought after species can fructify, if it is cultivated, in a deep cellar at all seasons of the year. The culture in cellars with the help of indefinitely grafted mycelium makes great modifications appear in the general form of the mushroom, and this to such an extent that certain characteristics of the blue-foot species have become progressively attenuated until at last they have entirely disappeared. The individuals have taken a very marked gigantic character; the hat of 4 cm. in diameter, the stalk from 15 to 18 cm. high, excessively thick and humidified. Also the violet tint so characteristic of this mushroom, from which it has taken its popular name of "blue foot," no longer exists neither on the stem which is white nor on the blades which are of a creamy colour, nor on the hat which is of a silky white hardly tinted with a very light shade of coffee and milk, which shade has progressively replaced the original nut-brown colour. The modifications of form and colour have not appeared all at once excepting as far as concerns the enormity of the stalk. M. Matruchoth concludes that these experiments teach us that the *Tricholoma nudum*, cultivated in cellars, in the dark, at 11°, in a normally hygrometric atmosphere, vegetates as vigorously as in a state of nature. The blue-foot being able to produce in all seasons gives a continuous harvest. Moreover, every winter the white mushroom can be grafted with the help of young filaments taken from a culture of the preceding year. Thus it is possible to perpetually renew the culture, which is not the case with the mushroom of ordinary beds that are cultivated in quarries. Lastly, the delicate taste and aniseed perfume of the blue-foot subsists integrally, which indicates that the profound chemical qualities of the cellulose is not sensibly modified. It is this same species that MM. Costantin and Matruchoth in previous researches had cultivated in the open air, but without obtaining a sufficient return.

AEROPLANES AND MARINE BIRDS.

For a year past Dr. Magnan, Director of the Ecole des Hautes Etudes, has been collecting very numerous documents concerning the flight of birds. In a most rigorous manner he has calculated the alar surface, the weight of the wings, the spread and breadth of the wing, the total length of several hundreds of birds, at the same time as he studied the method of flight employed by the bird that he

was studying. He has remarked that the different relative dimensions were, as it were, constant for the same diurnal birds practising the same kind of flight. Thus all diurnal birds of prey have very sensibly the same alar surface; the relation of their wing spread to the length of their body is, so to say, constant. On the other hand, these dimensions differ considerably when one examines different groups of birds, as rapacious birds, palmipeds, marine birds, sparrows, &c. In seeking for the characteristics of marine palmipeds he has been able to define these characteristics thus:—Marine palmipeds possess the largest relative wing spread of all birds; on the other hand, they possess, so to say, the narrowest wing. Their alar surface is very great, though less than that of the rapacious birds. Their tail is considerably shortened. Their total length is about the same as that of birds of prey in spite of the shortness of the tail. Lastly, the relation between the spread and the width of the wing is the greatest. M. Magnan shows, moreover, that the narrowness of the wing and the shortening of the tail seem to be the consequence of an adaption to the flight in the great currents of air, since all aquatic birds (ducks, little waders) that fly in like conditions, have also a narrow wing and a short tail. M. Magnan had already proved by his study on hovering birds that it was possible to apply to aeroplanes the dimensions found by him in birds, and to make practical applications of the same. It is thus that the Pomier monoplane piloted by Vedrines in the race for the Gordon-Bennett cup in 1913 was the first application, and, at the same time, the justification of these researches. The fuselage (yards, &c.) of this monoplane present absolutely personal characteristics; according to the indications resulting from the work of M. Magnan it has the weakest relation of the total length to the spread. This reduction of the fuselage has permitted very rapid risings from the ground, and seems to give a superior ascensional force, since the avion of the Biclovucie cavalry type has attained the height of 1500 metres in five minutes. M. Magnan has calculated (as for the hovering apparatus copying the rapacious birds) the dimensions of a monoplane that would copy marine birds. He has found for an apparatus weighing 400 kilograms, in marching order:—

	Hovering monoplane, rapacious type.	Monoplane, type of marine birds.
Alar surface	12'60 metres	10'20 metres
Weight of wings	78'800 kilograms.	77'800 kilograms.
Spread	9'78 metres	10'30 metres
Width of wings	1'69 metres	1'25 metres
Length of tail	1'90 metres	1'32 metres
Length of the apparatus	4'34 metres	4'26 metres

As will be seen, there are very notable differences between these two types. It might perhaps be advisable for builders to take these data into consideration in totality or partially for the construction of hydroplanes.

COOLING OF THE EARTH.

A French mathematician, M. A. Veronnet, has just made a series of ingenious calculations, the aim of which was to determine the evolution and the duration of the earth. This is a question that for a long time past has been haunting the minds of seekers. Is the earth to finish her existence by meeting, in her vagabond course, some wandering planet? Is a formidable shock to scatter into space the earthly continents in an infinite number of fragments? This is one of the numerous hypotheses that have been considered by scientific men. Other theories have, however, been brought forward. For certain students the disappearance of the carbonic acid of the air would cause the cooling of the earth, and the consequent disappearance of all animal and vegetable life. For others, again, it is the water that would disappear from the surface of the globe, and our globe is thus destined to die from drought. But the most general opinion is that the earth will die of cold when the sun can no longer send us the beneficent

heat brought to us by its rays. Since the earth solidified the flux of internal heat is very weak, and its temperature at the surface depends almost entirely on the heat received from the sun. Now, in past times, when a ray of sun attained one and a-half the power of the present rays of sun—which must have been the case about two millions of years ago—the temperature must have reached 90° at the latitude of 80° . The appearance of life cannot go beyond that period, and according to M. Veronnet it must have begun in the proximity of the poles. M. Veronnet has also calculated that in a little less than two millions of years a ray of sun being reduced by about only one-tenth, the temperature will have fallen on the earth to below zero even at the Equator. The surface of the earth will be completely frozen, and life on it will be almost impossible. According to this same scholar the planet Mars has been thus frozen for a long time past. Thus the dreams of astronomers and poets who affirm that Mars is inhabited are disappointed. Mars is a block of ice, according to mathematicians, and the earth has only two millions of years to live. Alas, this conclusion is not very consoling.

COAL IN THE WORLD IN 1913.

The production of coal in the whole world, according to the last official statistics, may be estimated for 1913 at 1250 millions of tons, compared with 1245 millions of tons in 1912, 1184 millions of tons in 1911, and 500 millions of tons in 1910. The greater part belongs to the United States, with about 40 per cent of the total production, Germany and England come next with 21 per cent each; then, in order of importance, France, Russia, Belgium, Austria, Hungary, and Holland. The European production for 1913 may be estimated at 550 millions of tons, the consumption of which may be reckoned in the following manner:—Consumption of the mines, 38 millions of tons, or about 7 per cent; metallurgy, 192,500,000 tons, or about 35 per cent; railways, 55 millions of tons, or about 10 per cent; stocks for navigation, 55 millions of tons, or about 10 per cent; gas and electric lighting, 44 millions of tons, or 8 per cent; industry, 82,500,000 tons, or 15 per cent; domestic consumption, 82,500,000, or about 15 per cent. As is seen by this it is metallurgy, industry, and domestic consumption that require the largest quantities of coal.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 12, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Note on a Functional Equation Employed by Sir George Stokes." By Sir JAMES STIRLING, F.R.S.

1. In a paper by Sir George Stokes "On the Intensity of the Light Reflected From or Transmitted Through a Pile of Plates" (published in the *Proceedings* for 1862, see his "Math. and Phys. Papers," iv., 148-9), the author orms and solves two functional equations, viz.:—

$$\phi(m+n) = \phi(m) + \phi(n) \{ \psi(m) \}^2 / \{ 1 - \phi(m)\phi(n) \},$$

$$\psi(m+n) - \psi(m)\phi(n) / \{ 1 - \phi(m)\phi(n) \},$$

these equations being treated as independent.

2. The main object of the paper of Sir George Stokes is physical, not mathematical; and the purpose of the present note is to call attention to mathematical points not explicitly dealt with by him, viz.:—

(a) The two functional equations are not independent, the second being capable of being deduced from the first.

(b) The results arrived at by Sir George Stokes may be derived from the first equation alone and constitute the

general solution of that equation. No such general solution of the second equation has been obtained.

"The Mercury Green Line $\lambda = 5461$ as Resolved by Glass and Quartz Lummer Plates and on its Zeeman Components." By Prof. J. C. McLENNAN and A. R. McLEOD.

"Electrical Condition of a Gold Surface during the Absorption of Gases and their Catalytic Combustion." By HAROLD HARTLEY.

At the suggestion of Prof. W. A. Bone, the author has carried out experiments on the electrical conditions of a gold surface during its absorption of hydrogen, carbon monoxide, and oxygen respectively, at temperatures between 300° and 400° , in order to establish certain data relative to surface combustion phenomena.

The results have proved (1) that the metal acquires a negative charge during the catalytic combustion of gases in contact with it (thus confirming previous unpublished observations by Bone and Makower), which effect is probably antecedent to the actual combustion, and primarily due to "occlusion" phenomena; (2) that the metal becomes negatively charged (0.5 to 1.5 volt) during the occlusion of the combustible gas (hydrogen or carbon monoxide), and positively charged (0.8 volt) during the occlusion of oxygen; and (3) that such electrical effects are probably due to occluded gas which is leaving (rather than entering) the surface. Any cause, such as a sudden lowering of the temperature, which would momentarily check the outflow of occluded gas, diminishes the intensity of the charge, whilst, conversely, a sudden diminution in the external gaseous pressure in the vicinity of the metal, temporarily increases it.

The experiments indirectly lend support to the view that the well-known electronic emission from incandescent solids is probably dependent upon the occlusion of gas.

"Diffusion of Electrons Through a Slit." By J. H. MACKIE.

The paper deals with a comparison of the solutions of the two equations—

$$\frac{\partial^2 n}{\partial x^2} = 2\lambda \frac{\partial n}{\partial z}$$

$$\frac{\partial^2 n}{\partial x^2} + \frac{\partial^2 n}{\partial z^2} = 2\lambda \frac{\partial n}{\partial z};$$

the value of n being subject to certain prescribed boundary conditions. The equations arise in connection with certain experiments by Prof. Townsend and Mr. Tizard on the Diffusion of Ions through Gases, and the comparison of the numerical solutions show under what conditions the term $\partial^2 n / \partial z^2$ can be neglected.

"Rate of Solution of Hydrogen by Palladium." By A. HOLT, D.Sc.

The rate of solution of hydrogen at constant (atmospheric) pressure by palladium in the form of black thin and thick foil has been examined. The rate curves in the case of palladium black are simple and of continuous curvature, but for the foil a more or less pronounced discontinuity of curvature is always observed.

The discontinuity is accounted for by considering that the gas is dissolved in two different forms of the metal, the rate of solution being different in the two forms. Palladium black is believed to consist almost wholly of one form, and hence gives a simple rate curve, whilst the foil (which is mainly crystalline) contains both varieties of metal, and so gives two rates, the first rate passing into the second when solution in both forms becomes equally rapid.

The nature of the two terms of the metal is discussed, and it is concluded that the difference lies in the ordered or haphazard arrangement of the metallic particles.

"Dispersion of a Light Pulse by a Prism." By R. A. HOUSTON, D.Sc.

A light pulse of a form giving the Wien energy distribution is incident on a prism, and expressions are derive

(1) for the disturbance in the region immediately behind the prism where the different colours overlap, and (2) for the disturbance in the focal plane of the telescope. The first expression holds only for a particular law of dispersion, but the second is for any law of dispersion. They are both in accordance with results obtained by Lord Rayleigh by considerations of stationary phase and hydrodynamical analogy, but they go further. For example, it is definitely stated how the amplitude varies in the front and rear of and throughout the train of waves given rise to by the pulse in the different parts of the spectrum.

CHEMICAL SOCIETY.

Ordinary Meeting, March 5, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President,
in the Chair.

(Concluded from p. 141).

65. "The Influence of Configuration on the Condensation Reactions of Polyhydroxy-compounds. Part I. The Constitution of Mannitoltriacetone." By JAMES COLQUHOUN IRVINE and BINA MARY PATERSON.

Mannitoltriacetone has been selected as a test substance in an endeavour to correlate the configuration of polyhydroxy-compounds with their capacity to enter into condensation with aldehydes or ketones. It was found that, when dissolved in aqueous alcohol containing minute quantities of hydrogen chloride, the ketonic residues could be removed from mannitoltriacetone in the definite stages indicated below:—

Mannitoltriacetone $\rightarrow$ mannitoltriacetone $\rightarrow$
mannitolmonoacetone $\rightarrow$ mannitol.

Mannitoltriacetone crystallises in needles melting at $37-39^\circ$, and has $[\alpha]_D +15.75^\circ$ in alcohol; on methylation it was converted into dimethylmannitoltriacetone (b. p. $140-141^\circ/13$ mm., $[\alpha]_D +21.9^\circ$), which, on hydrolysis, gave dimethylmannitol (needles, m. p. 93° , $[\alpha]_D -8.85^\circ$). This compound, on oxidation with nitric acid, was converted into dimethylmannonic acid, which was isolated in the form of the corresponding lactone (m. p. $112-114^\circ$).

In a parallel series of reactions, mannitolmonoacetone (needles, m. p. 85° , $[\alpha]_D$ in alcohol $+23.2^\circ$) was converted into tetramethylmannitolmonoacetone (b. p. $138-140^\circ/11$ mm., $[\alpha]_D +32.2^\circ$), from which tetramethylmannitol was obtained. The compound boiled at $167-169^\circ/13$ mm., showed $[\alpha]_D -12.54^\circ$ in alcohol, and gave, on oxidation with nitric acid, a tetramethylmannonic acid (b. p. $180-182^\circ/12$ mm.) incapable of forming a lactone.

It was also found necessary to examine the form of tetramethylmannitol obtained by the reduction of tetramethylmannose. The compound thus produced boiled at $177^\circ/11$ mm., and showed $[\alpha]_D +39.8^\circ$ in alcoholic solution, and is thus isomeric with the product obtained by the hydrolysis of tetramethylmannitolmonoacetone. Moreover, on oxidising tetramethylmannose by means of bromine, a second form of tetramethylmannonic acid was isolated, which was readily transformed into tetramethylmannono-lactone (b. p. $174^\circ/11$ mm., $[\alpha]_D +78.8^\circ \rightarrow 38.5^\circ$ in aqueous alcohol).

From these results the following conclusions are drawn:—(1) In mannitoltriacetone the ketonic residues are symmetrically linked to α -carbon atoms; (2) the stabilities of the three residues are unequal; (3) the least stable residue is linked to a primary alcoholic group; (4) the most stable residue is linked to the remaining primary alcohol group.

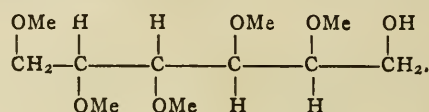
66. "The Formation of Ethers from Mannitol. An Example of Steric Hindrance." By JAMES COLQUHOUN IRVINE and BINA MARY PATERSON.

In attempting to prepare mixed ethers by the alkylation of dimethyl- or tetramethyl-mannitol, it was found that the reaction was completely arrested at a stage when a penta-

substituted derivative was formed. Thus, 3:4:5:6-tetramethylmannitol, when subjected to the action of silver oxide and ethyl iodide, was converted into the corresponding tetramethylethylmannitol (b. p. $140^\circ/8$ mm.), and, in a parallel reaction in which methyl iodide was used, the product consisted of pentamethylmannitol (b. p. $137-138^\circ/8$ mm.). As the latter compound was converted, on oxidation with nitric acid, into a pentamethylmannonic acid (b. p. $110^\circ/0.18$ mm.), the resistance to methylation was evidently presented by one of the terminal hydroxyl groups.

Notwithstanding the configuration symmetry of mannitol, the remaining primary alcohol group behaved in a different manner, and was readily methylated.

The combined results of the research support the view, expressed in the preceding communication, that the terminal alcohol groups in mannitol preferentially assume fixed positions, with the result that three adjacent hydroxyl groups are arranged on the same side of the carbon chain. Only two of these three groups undergo methylation, and the stereochemical formula of pentamethylmannitol is as follows:—



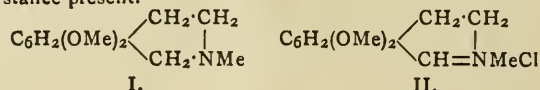
As the silver oxide method of methylation has frequently been employed to discriminate between different types of sugar derivatives, it was necessary to apply the process to 2:3:5:6-tetramethylmannitol in order to ascertain if the secondary alcohol group resisted substitution. The reaction yielded the pentamethylmannitol described above, so that the previous conclusions regarding constitution in the sugar group, which are based on the methylation process, are not affected adversely by the results of the present investigation.

The specific rotations of the partially methylated mannitols now described display a number of regularities from which it is possible to allocate a qualitative rotatory power to each of the four asymmetric systems in mannitol.

67. "The Relative Strengths of Ammonium and the Substituted Ammonium Hydroxides as Measured by their Action on a Pseudo-base." Part I. By CHARLES KENNETH TINKLER.

The method employed depends on the spectroscopic determination of the amount of the ammonium form of a pseudo-base converted into the corresponding carbinol by the action of a soluble base. 1-Hydroxy 6:7-dimethoxy-2-methyltetrahydroisoquinoline has been employed as the pseudo-base.

By comparing the ultra-violet absorption spectra of the pseudo-base, in a solution of a soluble base, with those of mixtures of known composition of the hydro compound (I.) and the chloride (II.), it is possible to estimate the amount of the carbinol and ammonium forms of the substance present.



The general result of the investigation is to show that the bases employed increase in strength in the order:—Ammonium hydroxide, trimethylammonium hydroxide, methylammonium hydroxide, dimethylammonium hydroxide, tetramethylammonium hydroxide, which is in accordance with the results obtained by other investigators.

The present investigation has also shown that the conversion of the ammonium form of the pseudo base into the carbinol is in accordance with the law of mass action; that is, concentration of ammonium form of pseudo-base $\times$ concentration of hydroxyl ion = $K \times$ concentration of carbinol.

Diaminomesitylene is readily converted into either aminomesitylenediazonium chloride or mesitylenebis-diazonium sulphate; the former salt yields aminomesitylenazo- β -naphthol (bright red needles, m. p. 173°), whilst the latter gives rise to mesitylenebisazo- β -naphthol (maroon-red nodules, m. p., indefinite, 270–275°). The

bisazo-derivatives can also be produced by successively diazotising the monoazo-compound and coupling with β -naphthol.

Other diazonium salts illustrating the two stages of diazotisation of diaminomesitylene are under examination, together with the corresponding triazides and the azo-dyes obtained by coupling the mono- and bis-diazonium salts with 2:4-tolylenediamine and other bases and phenols.

74. "The Variable Rotatory Powers of the *d*- α -Bromocamphor- β -sulphonates." By WILLIAM JACKSON POPE and JOHN READ.

In applying *d*- α -bromocamphor- β -sulphonic acid to the resolution of externally compensated bases, the authors have observed discrepancies amongst the molecular rotatory powers of the salts obtained; they now trace the latter to the occurrence of dynamic isomerism in the acid, and have been able to isolate stereoisomeric ammonium *d*- α -bromocamphor- β -sulphonates which exhibit the molecular rotatory powers $[\text{M}]_{5461} + 271^\circ$ and $+176^\circ$.

75. "The Optical Activity of Compounds of Simple Molecular Constitution. Ammonium *d*- and *l*-Chloriodomethanesulphonates." By WILLIAM JACKSON POPE and JOHN READ.

The authors have prepared externally compensated chloriodomethanesulphonic acid, $\text{CHCl} \cdot \text{SO}_3\text{H}$, and have resolved it into its optically active components by crystallisation with *d*- and *l*-hydroxyhydrindamine, brucine, and strychnine. Ammonium *d*-chloriodomethanesulphonate has the molecular rotatory power $[\text{M}]_{5461} + 43.7^\circ$ in aqueous solution; the optical activity is very persistent, and the salt does not undergo racemisation when its aqueous solution is heated in a sealed tube at $136-150^\circ$.

76. "The Lower Limits of Inflammation of Methane with Mixtures of Oxygen and Nitrogen." By ALBERT PARKER.

The lower limits of inflammation of methane have been determined, when mixed with pure oxygen, when mixed with oxygen (80 per cent) and nitrogen (20 per cent), and so on down to an admixed gas containing only 13.5 per cent of oxygen. The mixtures were sparked in a spherical glass vessel of 2.5 litres' capacity, the lower-limit mixture being taken as the one containing the smallest quantity of methane, in which the flame travelled throughout. With pure oxygen, the lower limit of methane is found to be 5.99 per cent, whereas with air the value is only 5.77 per cent. The most probable explanation of the higher value for oxygen is that the specific heat of oxygen is greater than that of nitrogen at the ignition-temperature of methane. A reduction in the oxygen content of the admixed gas from 20 to 13.5 per cent causes an increase in the lower limit of methane to 6.29 per cent.

PHYSICAL SOCIETY.

Ordinary Meeting, March 13, 1914.

Dr. A. RUSSELL, Vice-President, in the Chair.

A PAPER entitled "Time Measurements of Magnetic Disturbances and their Interpretation" was read by Dr. C. CHREE.

The paper is a sequel to one read before the Society in November, 1910 (*Proc.*, xxiii., 49), dealing with the times of commencement of fifteen magnetic disturbances discussed by Mr. R. L. Faris, and supposed by him to support Dr. L. A. Bauer's theory that the commencing movements of magnetic storms travel round the globe at rates of the order of 100 km. per second. In his previous paper the author criticised Mr. Faris's paper, and suggested that for an adequate test of Dr. Bauer's theory data could only be obtained from a number of stations encircling the earth. Shortly afterwards Dr. Bauer issued a circular requesting magnetic observatories to send him their

measurements of the times of commencement of the fifteen magnetic storms discussed by Mr. Faris. Upwards of thirty stations sent in data in answer to Dr. Bauer's request. A discussion of the data derived from the horizontal force curves has recently been published by Dr. Angenheister, whose conclusions are unfavourable to Dr. Bauer's theory. The present paper deals with the data from the declination and vertical force curves as well as those from the horizontal force curves following a somewhat different method from that adopted by Dr. Angenheister. The bearing of the data on Dr. Bauer's theory is discussed, and the peculiarities of the individual stations are considered.

DISCUSSION.

Prof. S. P. THOMPSON thought that Dr. Chree's conclusions pointed to the necessity of equipping all magnetic observatories with similar instruments and making them keep records to a tenth of a second.

Mr. R. S. WHIPPLE mentioned the enormous amount of work involved in the reduction of these observations. The instrumental errors due to backlash and other causes were apt to be so great that it was really marvellous that observers went so far as to discuss times of the magnitude involved. He emphasised the need of standardised instruments.

Prof. C. H. LEES said that, like most people who had read Dr. Bauer's paper when it appeared, he had had grave doubts of the instrumental accuracy. He thought the method of calculating the results rather biased. He had set a student to work out the correlation number of the times of the disturbances and the longitudes of the observatories. The number was too small to justify any conclusion as to connection between the quantities.

Mr. C. W. S. CRAWLEY thought it would be an advantage to work on a much larger time scale, say, 2in. or 3in. per minute, and make use of the little everyday disturbances. He had observed a large number of these in this way. Sometimes the disturbance commenced with a contrary kick and sometimes it did not. The phenomenon, when present, was quite easy to detect. He asked Dr. Chree if no connection ever existed between disturbances and volcanic action.

Dr. A. RUSSELL asked the author if it was known whether atmospheric gales had any effect in producing magnetic storms. It was well known that in the Arctic and Antarctic regions violent magnetic storms were of frequent occurrence. These were often attributed to swarms of electrons flying past the earth. If this were so it would be possible for vortex rings of electric current to be set up which would travel comparatively slowly round the surface of the globe. These might conceivably alter the force components of terrestrial magnetism. In his opinion, the possible effects of the currents existing in the interior of the earth, or set up on its surface by celestial disturbances, ought to be considered as well as the currents in the upper atmosphere.

The AUTHOR, in reply, stated that the objection to using a wide time-scale was that an enormous amount of photographic paper would be necessary. Moreover, if the scales are too open, the curves present such a large number of features demanding attention that the staff usually at the disposal of an observatory would be unable to cope with the work involved. The objection to using the small disturbances, which were quite frequent, was the difficulty of ensuring that all the observers were dealing with the same disturbance. Dr. Moos had suggested a connection between certain magnetic disturbances and volcanic action, but he did not think the evidence was conclusive. Dr. Leyst, of Moscow, had established a relation between the amplitude of the ordinary magnetic variations and the height of the barometer.

A paper "On the Ratio of the Specific Heats of Air, Hydrogen, Carbon Dioxide, and Nitrous Oxide" was read by H. N. MERCER.

The main object of the experiments was to test the

accuracy with which γ could be measured, employing small quantities of the gas, with the ultimate view of experiments on the variation of γ with temperature. The method employed was to observe with a platinum thermometer of very fine wire the instantaneous fall of temperature corresponding to a given rapid fall of pressure. The method was first employed by Lummer and Pringsheim ("Smithsonian Contributions," 1898), using a bolometer strip, with a vessel of 50 to 100 litres capacity. It was later employed by Makower (*Phil. Mag.*, February, 1903) for the determination of γ for steam, with modifications introduced by Prof. Callendar, which consisted in the substitution of a platinum thermometer, compensated for conduction along the leads, in place of the bolometer strip, and in the adoption of an automatic contact for closing the galvanometer circuit at the right moment, which made it possible to work with smaller quantities of gas. The vessel used by Makower was about 9 litres in capacity. The apparatus employed in the present experiments was similar to that used by Makower, but it was found that with due precautions an equal degree of accuracy was obtainable with a vessel of only 300 cc. capacity.

A table is given in the paper showing the values of the specific heat at constant pressure for the various gases as calculated from the present experiments. The values show good agreement with direct calorimetric determinations.

DISCUSSION.

Prof. C. H. LEES thought the paper marked an advance in the subject. Hydrogen was always a severe test in such measurements, and the corrections were troublesome.

Mr. F. E. SMITH asked what was the diameter of the platinum wire used, as there was probably a lag between its temperature and that of the gas. He thought more information was required on the time of making the galvanometer contact. It was possible that the gas might have commenced to cool, and in consequence to lower the temperature of the thermometer, before the correction due to the heating current had attained its final value.

The AUTHOR stated that the wire was very fine, about a fortieth of a mm. in diameter, and he did not think there could be an appreciable lag.

A paper entitled "*The Asymmetric Distribution of the Secondary Electronic Radiation produced by X-Radiation*," by A. J. PHILPOT, as taken as read.

Homogeneous X-radiations, characteristic of various elements, have been employed to eject electrons from gold. By an ionisation method the relative energies of the electrons emitted in the direction of propagation of the exciting X-radiation and in the reverse direction have been measured for each of the homogeneous X-radiations employed. It has been found that the ratio of the energy of the former to that of the latter increases with the penetrating power of the exciting radiation, its value rising from 1.11, when the mass absorption coefficient of the X-radiation was 5.0, to 1.24, when the mass absorption coefficient was 0.5.

A paper entitled "*A Lecture Experiment on the Irrationality of Dispersion*" was read by Prof. S. P. THOMPSON.

Newton's method of crossed prisms throws an oblique spectrum on the wall. If the prisms used are of identical kinds of glass the oblique spectrum is straight from red to violet. But if different kinds of glass are used, the spectrum is curved by reason of the irrationality of dispersion in one or both of the glasses. If a diffraction grating is used instead of one of the prisms, then the curvature which is observed is that resulting from the irrationality of dispersion of the particular prism employed, and for all known kinds of glass the refraction for blue and violet rays is disproportionately large. To exhibit these effects in the lecture theatre a diffraction grating of 12,000 lines to the inch is employed to cast on the screen a horizontal spectrum of the first order, the light from an arc lamp being sent through a small round or square hole. On interposing a prism to disperse the light vertically

upwards, the resultant oblique spectrum is finely curved, being concave upwards. If in the arc lamp the carbons used are those supplied for commercial "flame arcs," the effect is more brilliant, since the spectrum contains several bright bands. If an alloy of zinc, thallium, and lithium is introduced into the crater of the positive carbon, a still more striking series of bright points is produced in the curved spectrum.

SOCIETY OF CHEMICAL INDUSTRY. (LONDON SECTION).

Ordinary Meeting, March 2, 1914.

Prof. W. R. E. HODGKINSON in the Chair.

THE following papers were read and discussed:—

"*Bleaching of Chemical Pulp and Suggestions for a Standard Method in Test Cases*." By ARTHUR BAKER and JAMES JENNISON.

The authors have studied the above more particularly from the industrial standpoint and with particular reference to:—

1. Rate of bleaching at constant temperature.
2. Rate of bleaching at varying temperatures.
3. Influence of residual bleach liquors upon the economy of the process.
4. Influence of preliminary acid or alkaline treatment.
5. Influence of the concentration of the pulp.

Conclusions arrived at by observations made during the carrying out of the above experiments are:—

(a) That the use of residual bleach liquor or back liquor is attended with an increase in the bleach consumption, and accompanied by a lowering of the colour of the resultant bleach pulp; the use of bleach back liquor only being justified in the washing of material prior to bleaching, when it can be thoroughly removed before the fresh bleach solution is added to the half stuff.

(b) That preliminary washing, either by water, dilute acid, or dilute alkali, is not worth while in the case of easy bleaching pulp.

(c) That the concentration of the pulp is the most important factor to be taken into consideration, and due regard to this point is absolutely essential in order to obtain the highest economy in the bleaching process as carried out in the paper mill.

(d) That a temperature of 120° F. should not be exceeded in any case.

As an outcome of the above experiments, and in view of the fact that Sindall and Bacon's suggestion to use tintometer readings as a method of stating colour values of bleached pulps has not met with any approval, we suggest for arbitration and specification purposes a standard bleaching test on the following lines:—

Minimum quantity of pulp to be taken 10 grms., 10 per cent air dry pulp, 160 cc. of water containing 12 per cent of bleach powder (35 per cent Cl) calculated on the 10 per cent air dry pulp. Temperature, 100° F.; time, two hours.

The pulp is obtained in a fine state of division for bleaching by agitating with a heavily designed brass stirrer of the egg-beater type fitted with teeth.

Samples of the resultant bleached pulp after washing are obtained by making small hand-made sheets, and air drying the same.

For standards of reference, and this has been the main difficulty, we suggest suitable colours be fixed by representatives of the Paper Makers' Association and the Wood Pulp Association. These standards to be official, and matched in dull porcelain as follows:—

- A. Colour obtained by first quality easy bleaching sulphite.
- B. Colour obtained by second quality easy bleaching sulphite.

C. Colour obtained by first quality easy bleaching sulphate.

D. Colour obtained by second quality easy bleaching sulphate.

Standards to be kept by the Paper Makers' Association and Wood Pulp Association of the various countries as official standards.

The percentage of bleaching powder required to give any of the proposed standard colours would under the conditions of the standard test serve as a direct indication of its value from a white colour point of view.

"Application of Calcium to the Formation of Alloys."

By W. R. HODGKINSON.

In connection with copper and some of its alloys a mixture of calcium carbide with borax, boric acid, common salt, or other chlorides was found a very efficient deoxidising flux. A considerable number of metallic oxides, e.g., CaO, ZnO, FeO, PbO₂, are reduced to metal when heated with carbide, but the reagent is not convenient for the purpose. Attempts to reduce oxides of such metals as cerium and zirconium and to form alloys by using a mixture of the metallic oxide, carbide, and copper powder or copper oxide were unsuccessful at ordinary furnace temperatures. Experiments with the chlorides either ready formed or formed *in situ* by introducing a mixture of the oxide and ammonium chloride in small portions at a time into a heated crucible (having regard to the possible volatilisation temperature of the chloride) were more successful.

Two methods for the production of alloys were used. In the former a mixture of halide, carbide, and the principal metal is used, whilst in the latter and better method both or all the metals are as halides. When the former method is used the mixture of dry halide with powdered carbide is dropped on to the principal metal already fused in a crucible, and after the whole is fused the contents are stirred once or twice and poured. When working with mixed halides the mixture with or without an additional flux is placed in a crucible already heated, or packed into the crucible cold and then fused. Much heat is evolved by the interaction of some halides, such as those of copper, lead, zinc, nickel, cobalt, and silver with carbide. This materially assists the reaction when certain of the halides or double salts are simultaneously employed.

Copper has in many cases been used as the principal element of the alloy to be formed. Alloys of this metal, with Co, Ni, Mn, Ce, Zn, Ta, Ti, were formed. The quantities of the four latter metals taken up in the alloy were in all cases less than the theoretical; with the others the loss was not so great; it would probably be less on a large scale.

Alloys of manganese are conveniently formed as the chloride melts without serious volatilisation at below 1000° C. Those containing Bi, Pb, Sn, Sb, Cu, Ag, Co, Ni have been prepared.

Metallographic details are reserved for a later communication.

"Blasting Gelatin, Some Notes and Theories." By W. A. HARGREAVES.

Blasting gelatin is officially defined as consisting of nitro-cotton, carefully washed and purified, combined with thoroughly purified nitroglycerin in such proportions that the whole shall be of such character and consistency as not to be liable to liquefaction or exudation, and with or without calcium carbonate or magnesium carbonate not exceeding 2 parts by weight in every 1000 parts of the finished explosive. In actual practice blasting gelatin consists only of nitroglycerin and nitro-cotton.

The author's experience as an inspector of explosives shows that manufacturers have not arrived at a knowledge of a definite proportion of nitro-cotton to use, and have never been certain of producing every time a blasting gelatin complying with the definition already mentioned. With the nitroglycerin there is no trouble, since it is a homogeneous liquid, and one that can be thoroughly washed and purified from all matters liable to confer instability

upon it. With nitro-cotton the case is different, there being always the possibility of small particles of impurity remaining in the cotton, surrounded and protected from the washing liquid by the colloidal matter of which the nitro-cotton is composed. Apart from the low-test difficulty there is the more common trouble of exudation of nitroglycerin. For this the usual remedy has been to increase the proportion of nitro-cotton. Four objections are stated to this:—(1) Risk of low-heat test; (2) the blasting gelatin likely to be insensitive to detonation by the ordinary No. 6 detonator; (3) considerable increase in generation of carbon monoxide; and (4) greatly increased cost.

Some years ago an hypothesis was formulated, and has been tested since by observation and experiments. This hypothesis is based upon the theory that blasting gelatin, instead of being a solution of a small quantity of nitro-cotton in a relatively large quantity of nitroglycerin, is really a colloidal solution of a certain quantity of nitroglycerin in nitro-cotton, intimately mixed with some free ungelatinised nitroglycerin.

After discussing this hypothesis the author suggests that the remedy for exudation is not to add more nitro-cotton, but to get a larger amount of gelatinisation during the initial mixing of the nitro-cotton and nitroglycerin, and to obtain this end more thoroughness is necessary in the preliminary mixing and also immediate and thorough working in a machine.

ALCHEMICAL SOCIETY.

ROGER BACON.

THE eleventh General Meeting of the Alchemical Society was held at the International Club, Regent Street, S.W., on Friday, March 13th. The Chair was occupied by the Acting President, Mr. H. Stanley Redgrave, B.Sc., F.C.S.

A very interesting lecture was delivered by Mr. B. RALPH ROWBOTTOM dealing with the life, thought, and influence of the English alchemist and philosopher, Roger Bacon. After stating that very little was known of the early events in Roger Bacon's life, the lecturer pointed out that two of the factors undoubtedly potent in the formation of his original and pregnant philosophy were his deep knowledge of mathematics acquired during his stay at Oxford, and his study at a slightly later period of the best Arabic writers. The fact was next emphasised that, although Roger Bacon was usually known to us as an alchemist, his great achievement was the creation of a system to be applied in the unravelling of the laws of nature, which was remarkably similar to that we to-day call scientific method. The lecturer proceeded to deal with several of Roger Bacon's works, pointing out the extremely short time in which the most important were written, and he finally gave the construction of the *Opus Majus* in detail. In conclusion, Mr. Rowbottom suggested that the day will probably come when the name of Roger Bacon will no longer call to mind magic or "spooks," but a man who, born into an ignorant age, shed a light not to be considered negligible even in the present century.

The lecture was followed by an animated discussion.

The full text of the lecture and an abstract of the discussion will be published in the March number of the Society's Journal.

Preparation by Catalysis of Decahydroquinoline and Decahydroquinoline. — Paul Sabatier and M. Murat.—Decahydroquinoline can be prepared by hydrogenation of quinoline over nickel; it is a colourless liquid with a very strong alkaline reaction. An excellent yield of decahydroquinoline, C₁₀H₁₉N, can be obtained by the direct hydrogenation of quinaldine over very active nickel. Like decahydroquinoline it turns red litmus blue, fumes in air, and combines with carbon dioxide, giving a solid carbonate. The authors have also prepared the chloroplatinate, acid oxalate, picrate, &c.—*Comptes Rendus*, clviii., No. 5.

NOTICES OF BOOKS.

The Elements of Qualitative Chemical Analysis. By JULIUS STIEGLITZ. Volumes I. and II. London: G. Bell and Sons, Ltd. 1914.

THE first volume of this book deals with the fundamental principles of qualitative analysis. Part I. contains a short outline of physical chemistry, which will probably be found sufficiently full for the student who has not already been through a course on the subject. Many references to larger works and to original papers are included, and those which are specially suited for the students' reading are distinguished from the others. The second part explains in detail the application of the general principles to the processes of qualitative analysis. In the second volume a complete course of qualitative analysis is given; this volume is interleaved with blank paper in order that the many questions which are scattered through the text may be answered in writing by the student, who will thus be helping to compile his own text-book. The book is a good example of a thoroughly modern work on qualitative analysis, and provides a valuable training in the scientific method of attacking analytical problems and in careful practical work.

Principles and Practice of Agricultural Analysis. Second Edition. Volume III. *Agricultural Products.* By HARVEY W. WILEY, A.M., Ph.D. Easton, Pa.: The Chemical Publishing Co. London: Williams and Norgate. 1914.

THE author of this book has made it his special aim to give a succinct account of the historical development of agricultural analysis, and to show clearly the present state of our knowledge of its principles and practice. The book will prove of considerable value as a work of reference, and the copious details it contains will enable the analytical chemist to select and carry out with success any of the methods usually employed in agricultural analysis. Much attention has been paid to continental literature on the subject, and many references are given to foreign periodicals. Special emphasis is laid upon the fundamental principles, and the first part gives a detailed description of general methods and apparatus. Subsequent sections deal with the extraction and identification of the various constituents of vegetable and animal products and the analysis of dairy products and feeding-stuffs, and the determination of nutritive values, &c., are fully treated.

Laboratoriums - Einrichtungen für Quantitative Analyse durch Elektrolyse. ("Laboratory Equipment for Quantitative Analysis by Electrolysis"). Aachen: Gebr. Raacke.

THIS catalogue of apparatus for the equipment of laboratories for quantitative analysis by electrolysis contains a detailed account of the laboratory of the Königl. Techn. Hochschule at Aachen, which was equipped by Messrs. Raacke, and was the first of its kind in Germany and a model for similar institutions. The catalogue contains an illustrated price list of various kinds of electrical heating and other apparatus.

La Nature des Rayons X. ("The Nature of the X-Rays"). By AUGUSTO RIGHI. Bologna: Nicola Zanichelli. 1914.

IN this lecture, delivered before the Congress of Italian Radiologists at Milan, Prof. Righi described, in the graphic and clear style of which he is a master, recent discoveries relating to the nature of the X-rays. After speaking of the early investigations of the rays, he explained in simple non-technical language the experiments which have been

performed on their reflection, and pointed out that the logical conclusion of these experiments is that the X-rays are of the same nature as light rays, and are thus a manifestation of electro-magnetic waves propagated in the ether.

Lectures on the Research Chemist in the Works, with Special Reference to the Textile Industry. By W. P. DREAPER. London: The Institute of Chemistry of Great Britain and Ireland. 1914.

THE two lectures contained in this book were delivered before the Institute of Chemistry in October and November, 1913. The lecturer discussed briefly the training required by the research chemist occupied in the textile industries, and the probable nature of the original work which he would be called upon to do. The equipment of the laboratory and the establishment of experimental works are considered, and some special problems are discussed to illustrate the general remarks. Many processes which are employed in the textile industries, such as embossing, waterproofing, silk weighting, &c., are treated, and research chemists, both those who are just entering upon their career and those who have had some years of experience, will find the lectures stimulating and interesting.

Tabellen zur Berechnung der "Theoretischen" Molrefraktionen Organischer Verbindungen. ("Tables for the Calculation of the 'Theoretical' Molar Refractions of Organic Compounds"). By K. v. AUWERS and A. BOENNECKE. Berlin: Julius Springer. 1914.

THIS handbook is issued as a supplement to Roth and Eisenlohr's book on refractrometry, and is designed to save the worker the lengthy and tedious calculations necessary for obtaining the values of molar refraction and dispersion. The tables include the hydrocarbons, substances containing oxygen and halogen derivatives, and they can also be used for any other elements if the atomic refractions of the latter are known. Only compounds containing up to 15 atoms of carbon are included, and no triple bond derivatives. In the calculations Eisenlohr's four-figure tables of atomic refraction have been used, except in the case of bromine, when results which are probably more accurate have been employed.

International Rubber Congress and Exhibition, Batavia (Java), 1914. Guide to Visitors.

THIS guide for visitors to the International Rubber Congress and Exhibition to be held at Batavia in September and October, 1914, contains much information relating to the Congress, including the titles of the lectures which will be given and the subjects which will be discussed. Many excursions to well-known rubber estates in West Java and elsewhere will be organised, and the attractions of the island combined with the interesting programme arranged will no doubt induce many experts and others interested in the preparation or cultivation of rubber to attend the Congress.

Sulphurous Anhydride and Camphor.—I. Bellucci and L. Grassi.—It has long been known that camphor readily absorbs large quantities of sulphur dioxide, giving a colourless liquid, which, when left in air, slowly evolves SO₂, and leaves the original camphor behind as residue. The determination of the melting-points of mixtures of the two substances in varying proportions indicates the formation of two compounds, namely, 2SO₂.C₁₀H₁₆O (m. p. -45°) and SO₂.C₁₀H₁₆O (m. p. -24°). The well-known fact that sulphuryl chloride is readily formed by the action of chlorine on SO₂ in presence of camphor is probably connected with the formation of these compounds.—*Atti della Reale Accad. dei Lincei*, xxii., [ii.], No. 12.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 6, February 9, 1914.

Velocity of Reaction in Catalytic Hydrogenations in presence of Platinum Black.—G. Vavon.—The velocity curves of the hydrogenations of substances capable of fixing several molecules of hydrogen show a very different appearance according to the quality and quantity of the catalyst. By heating platinum black its activity may be diminished, so that it becomes unable to effect difficult hydrogenations, while it may still easily catalyse less difficult hydrogenations.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvii., No. 2, 1914.

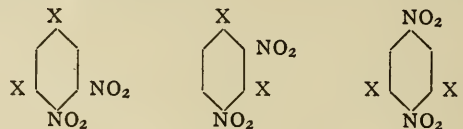
Synthetic Rubber from Isoprene.—G. Steimmig.—Harries has stated that the synthetic rubber prepared from isoprene by heating, and also by acetic acid polymerisation, is chemically identical with para rubber, there being no differences in the derivatives of the two substances. Both are supposed to be composed of the same hydrocarbon, 1.5-dimethyl-cyclooctadiene-1.5. Similar polymerisation products of isoprene have been obtained by heating it in presence of ozonides or peroxides, or by acting upon it with sodium in presence of carbon dioxide. These products yield ozonides from the decomposition of which succinic acid and acetyl acetone result. These two decomposition products must be formed from 1.6-dimethyl-cyclo-octadiene-1.5, and thus rubber prepared artificially from isoprene must consist of a mixture of 1.5- and 1.6-dimethyloctadiene-1.5. The product obtained by Harries gives a similar result. The formation of these two isomeric rings is clearly caused by the asymmetrical structure of isoprene. Natural rubber gives no derivative of 1.6-dimethylcyclooctadiene-1.5, and is thus a single substance. This explains why all rubber-like products artificially obtained from isoprene are not identical in properties with natural rubber.

Tungsten Cyanide.—Arthur Rosenheim and Eitel Dehn.—The authors have prepared a cadmium-triammin salt of the tungsten cyanide anion, $[\text{Cd}(\text{NH}_3)_3]_2[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$, analogous to the cyanide of molybdenum, $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$. They have shown by titration with permanganate that in this compound tungsten behaves like a pentavalent element, and it is thus, like molybdenum, an exception to the valency rule.

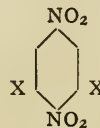
Atti della Reale Accademia dei Lincei.
Vol. xxii. [ii.], No. 12, 1913.

Reduction of Aldehydes to α -Glycols.—R. Ciusa and A. Milani.—When aldehyde is treated with magnesium amalgam three different reactions may occur:—(a) Reduction to primary alcohol. (b) Reduction to dissecondary α -glycol. (c) Condensation to aldol and subsequent reduction to β -glycol. These reactions proceed with different velocities, and the relative quantities of the products depend upon the velocities. In the case of the aldehydes of the fatty series the last reaction occurs most rapidly, and the β -glycol is the principal product. To prepare 2.4-butylenic glycol an ethereal solution of acetic aldehyde is made, and 2 per cent magnesium amalgam is added in very small portions. The ethereal solution is acidified with dilute sulphuric acid, washed, dried, and distilled. The portion coming over between 180° and 190° is redistilled, when the pure glycol passes over at 184 – 186° . Propionic and benzoic aldehydes may be treated similarly.

Dinitro Derivatives of Meta-dihalogen Benzenes.—G. Körner and Dr. Contardi.—The authors have extended their study of the dinitro derivatives of meta-dihalogen benzene by preparing and investigating the properties of the following:—



where X is a halogen. They have also obtained dinitro bromo-chloro, chloroiodo, and bromo-iodo derivatives of formula—



Vol. xxiii. [i.], No. 1, 1914.

Distillation of Nitroglycerin at a Low Temperature.—D. Chiaraviglio and O. M. Corbino.—The authors have devised an apparatus in which nitroglycerin can be distilled at a low temperature. By means of this apparatus they found it possible to distil about 10 grms. between 25° and 0° , the operation lasting about forty-four hours. From the data obtained the vapour pressure at 25° could be calculated from the formula $p = \sqrt{\frac{2\pi RT}{M}} m$, where R is the gas constant, T the absolute temperature, M the molecular weight, and m the quantity of the substance.

MEETINGS FOR THE WEEK.

- MONDAY, 30th.—Royal Society of Arts, 8. (Howard Lecture). "Surface Combustion," by Prof. W. A. Bone, F.R.S.
- TUESDAY, 31st.—Royal Institution, 3. "Landscape and Natural Objects in Classical Art," by A. H. Smith, M.A.
- Royal Society of Arts, 4.30. "Oil Resources of the Empire," by Dr. F. Mollwo Perkin.
- WEDNESDAY, April 1st.—Royal Society of Arts, 8. "Sarawak," by Her Highness The Rane of Sarawak.
- Society of Public Analysts, 8. "Damage caused to Vegetation by Sulphurous and Sulphuric Acids in the Atmosphere," by R. R. Tatlock and R. T. Thomson. "Abnormal Refraction of Milk Serum," by J. McCrae. "Water of Dorton Spa," by C. A. Mitchell.
- THURSDAY, 2nd.—Royal Institution, 3. "The Progress of Modern Eugenics," by C. W. Saleeby, M.D., &c.
- Royal Society, 4.30. (Bakerian Lecture). "Series Lines in Spark Spectra," by Prof. A. Fowler, F.R.S.
- Chemical, 8.30. "The System: Ethyl Ether—Water—Potassium Iodide—Mercuric Iodide; Part III., Solutions Unsaturated with Respect to Solid Phases in the Four component System," by A. C. Dunningham. "Velocity of Saponification of Acyl Derivatives of Phenols—Part I., Velocity of Saponification of Phenyl Benzoate," by H. McCombie and H. A. Scarborough. "General Method for the Preparation of Glyoxals and their Acetals," by H. D. Dakin and H. W. Dudley. "Action of Sulphuric Acid on *p*-Formaldehyde," by J. G. M. Dunlop. "Constitution of the Glycerolphosphates—Synthesis of α - and β -Glycerolphosphates," by H. King and F. L. Pyman. "Destructive Distillation of Soil," by E. J. Holmyard. "Addition Products of Nitro-compounds and Amines," by H. Housley. "Dibenzoylglucosylxose, $\text{C}_{11}\text{H}_{18}\text{O}_{10}(\text{CO} \cdot \text{C}_6\text{H}_5)_2 \cdot \text{H}_2\text{O}$, A Natural Benzoyl Derivative of a New Disaccharide," by F. B. Power and A. H. Salway.
- FRIDAY, 3rd.—Royal Institution, 9. "Further Researches on Positive Rays," by Prof. Sir J. J. Thomson, F.R.S.
- SATURDAY, 4th.—Royal Institution, 3. "Recent Discoveries in Physical Science," by Prof. Sir J. J. Thomson, O.M., F.R.S.

THE CHEMICAL NEWS.

VOL. CIX., No. 2836.

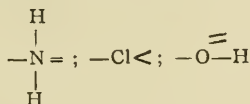
AN ENQUIRY INTO THE CONSTITUTION OF THE BENZENE NUCLEUS WITH REFERENCE TO THE PHENOMENON OF DI-SUBSTITUTION.

By CECIL L. HORTON.

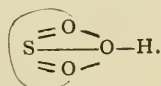
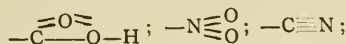
THE rule governing di-substitution is usually referred to as Crum Brown's rule, and reads—"If monosubstituent A is such that HA can be readily oxidised to HO.A the di-compound will be *meta*; otherwise *para* and *ortho*. Generally in the latter case *para* predominates." A list of the commoner radicles is given below in the appropriate column:—

<i>o</i> and <i>p</i> .	<i>m</i> .
NH ₂	C=O
NH—	C—OH
—OH	NO ₂
Cl	CN
Br	SO ₃ H
I	

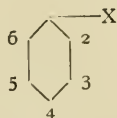
It will be noticed that each of the radicles in the first column is unsaturated:—



while those in the *m* column are saturated:—

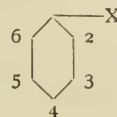


The effect of an unsaturated group displacing a hydrogen in the nucleus is to alter the distribution of the valency thus:—More of the valency of C₁ is absorbed by X leaving C₂ with an excess, which in turn takes more than its usual share from C₃. In C₄, owing to the shortage on C₃, has an excess. C₂ and C₄ will be more reactive than C₃. "Steric hindrance" will account for the predominance of the *para* di-substituted compound over the *ortho*.

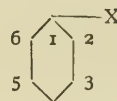


In the case of a saturated group it is extremely improbable that the distribution of the valency of the carbon at the junction is the same in the case of such a group as in the case of hydrogen. The heavily saturated element probably has only a minimum valency free to bind it to the carbon, and, therefore, the carbon to which the group is attached has more than the usual amount of valency to distribute to C₂ and C₆, and hence the valency of C₂ is distributed unevenly between C₁ and C₃, the smaller amount going to C₃. The same applies to C₆ and C₅.

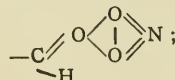
C₃ and C₅ have valency which cannot be entirely satisfied, by C₄, and hence the *m* position is the reactive one.



With regard to the behaviour of methyl, ethyl, &c. benzene, which compounds, while possessing as apparently saturated side chain, yet fall in the first of the groups mentioned, the following explanation is offered. Werner accounts for the existence of triphenyl-methyl on the grounds that C₆H₅ absorbs more of the carbon valency than does H, and therefore (C₆H₅)₃C is less saturated than is CH₃. Applying this principle we have that the carbon to which the alkyl group is attached has less than normal amount for C₂ and C₆, i.e., it behaves as if the alkyl group were unsaturated, since it gives more than the usual share to the carbon in the side chain.



Side chains of the type C=O, i.e., aldehydes and aromatic ketones, behave in an exceptional fashion. The radicle is essentially unsaturated, and yet the compounds formed by direct nitration are of the *meta* variety. Such an occurrence is best explained on the basis of an intermediate compound—



the radicle is thus saturated, and the NO₂ migrates to the *meta* position.

RELATIONS BETWEEN THE ROTATORY POWERS OF THE MEMBERS OF HOMOLOGOUS SERIES.*

By ROBERT HOWSON PICKARD and JOSEPH KENYON.

ATTEMPTS to discover a connection between the rotatory power and chemical constitution of a compound have been numerous since Crum Brown and Guye independently, in 1890, brought forward the theory connecting mass and molecular rotatory power. This now discarded theory has stimulated a large amount of research, the results of which up to 1904 have been summarised by Walden (*Ber.*, 1905, xxxviii., 345) and since then up to 1912 by Frankland (*Journ. Chem. Soc.*, 1912, ci., 654). The comparative failure (as regards the solution of the problem under consideration) of all this painstaking and laborious work led the present authors to plan a fresh investigation of the problem. Their results are as yet very incomplete, and have so far yielded no definite solution of the problem, but are put forward as a basis of discussion, as they appear to indicate some (at least) of the causes of the comparative failure of the earlier investigations. (See *Journ. Chem. Soc.*, 1911, xcix., 45; 1912, ci., 620 and 1427; 1913, ciii., 1923; 1914, cv., 94; *Proc. Chem. Soc.*, 1912, xxviii., 42; 1913, xxix., 296; *Ber.*, 1912, xlv., 1592.)

Previous investigators have studied as a rule the effect of various substituents on the rotatory power of some one optically active compound—in the great majority of cases,

* A Contribution to a General Discussion on "Optical Rotatory Power," held before the Faraday Society, March 27, 1914.

the effect of substituting the alcoholic or carboxylic hydrogen atoms in tartaric, glyceric, and malic acids and in borneol and menthol. It is highly significant, in view of some of our later results, that, almost without exception, the homologous series mentioned in the two summaries quoted above are all composed of esters, a class of compounds which it would now appear are particularly prone to exhibit *anomalous* rotatory dispersion. To this, and to the once universal custom of determining the rotatory power for sodium light only, as well as to the very frequent disregard of the effects of temperature and even of solvents, a great deal of the present confusion in the interpretation of the older results is most probably due.

When planning a reinvestigation of this problem, the authors determined to synthesise and examine optically active compounds of the simplest possible chemical constitution, each containing only one asymmetric carbon atom and, as far as possible, having the various radicles (the effect of which on the rotatory power was to be studied) attached directly to it. At first it appeared desirable to restrict the investigation to the examination at different temperatures of homogeneous liquids, but it has since been found that some well-marked relations (due solely to the molecular configuration) which exist between the rotatory powers of the members of some series could only be observed in solution, as they are masked at all temperatures up to the boiling-point when the compounds are examined in the homogeneous state.

So far there have been synthesised and systematically examined about forty secondary alcohols and some ninety esters derived from them. These are all of the general formulæ $R_1\cdot CH(OH)\cdot R_2$ and $R_1\cdot CH(O\cdot CO\cdot R_3)\cdot R_2$, respectively, where R_1 , R_2 , R_3 are normal alkyl radicles and comprise the following eleven homologous series of optically active compounds:—

- i. The carbinols of the series $CH_3\cdot CH(OH)\cdot R$, hereafter called the "methyl" series.
- ii. The acetates of these carbinols, $CH_3\cdot CH(O\cdot COCH_3)\cdot R$.
- iii. The dodecoates of the same, $CH_3\cdot CH(O\cdot COC_{11}H_{23})\cdot R$.
- iv. The esters of butan- β -ol, $CH_3\cdot CH(O\cdot COR)\cdot C_2H_5$.
- v. The esters of pentan- β -ol, $CH_3\cdot CH(O\cdot COR)\cdot C_3H_7$.
- vi. The esters of hexan- β -ol, $CH_3\cdot CH(O\cdot COR)\cdot C_4H_9$.
- vii. The esters of heptan- β -ol, $CH_3\cdot CH(O\cdot COR)\cdot C_5H_{11}$.
- viii. The esters of octan- β -ol, $CH_3\cdot CH(O\cdot COR)\cdot C_6H_{13}$.
- ix. The esters of undecan- β -ol, $CH_3\cdot CH(O\cdot COR)\cdot C_9H_{19}$.
- x. The carbinols of the series $C_2H_5\cdot CH(OH)\cdot R$, hereafter called the "ethyl" series.
- xi. The carbinols of the series $(CH_3)_2CH\cdot CH(OH)\cdot R$, hereafter called the "isopropyl" series.

Each of the compounds comprising these series contains only one asymmetric carbon atom and is of the simplest possible chemical constitution, this latter being moreover similar for all the compounds.

The relation between the rotatory powers of the members of these series can be readily explained in a qualitative sense by a consideration of the size of (or space occupied by) the radicles attached to the asymmetric carbon atom. Thus, representing the compounds by the symbols $abcd$, the effect of increasing the size of d (representing the "growing chain" in a series), is to alter in a more or less regular manner (usually to increase) the molecular rotatory power of the compounds. In the "methyl" series the space occupied by a , b , and c is the smallest conceivable (CH_3 , H , OH), and the values of the molecular rotatory power when measured in the homogeneous state increase regularly by small increments as the chain grows. In solution (ethyl alcohol and benzene), however, the rotatory powers of individual members of the series are considerably exalted when the whole molecule itself approximates in configuration to a ring structure, as in pentan- β -ol and decan- β -ol, or when the growing chain in a similar manner all but returns on itself, as in methyl amyl carbinol (heptan- β -ol) and methyl decyl carbinol (dodecan- β -ol). When, however, the space occupied by the groups or atoms represented by a , b , and c is larger,

the increase in molecular rotatory power, as d increases, becomes less regular. Either (1) it may be specially affected when the chain returns on itself, as in the "ethyl" series, where ethyl amyl, ethyl decyl, and probably ethyl pentadecyl carbinols (both in the homogeneous state and in solution) have values for the molecular rotatory power which are above those of the immediately preceding and succeeding members of the series, or (2) the increase may be relatively large until the growing chain d contains five carbon atoms with an increase of a much smaller order in the molecular rotatory power of successive members. This, for example, occurs in all the series of esters (except Nos. ii. and iii.) mentioned above, in which there is a rapid increase in the value of the molecular rotatory power $[M]_D^{20^\circ}$ for each member of the series up to the valerate, and a still further, but relatively much smaller, increase for each member from the valerate to the stearate when these are examined in the homogeneous state at 20° . When, however, the space occupied by the groups a , b , and c is still greater, the "approximate maximum" is reached when the growing chain contains fewer than five carbon atoms. Thus in the series of dodecoates, where the group $—O\cdot CO\cdot C_{11}H_{23}$ is large, the molecular rotatory powers increase in value rapidly up to that for $C_4H_9\cdot CH(O\cdot COC_{11}H_{23})\cdot CH_3$ with a much smaller increment beyond. Results of a similar character have been observed in the "isopropyl" series of carbinols. When examined in the homogeneous state, the member containing four carbon atoms in the growing chain has the conspicuous value for the molecular rotatory power; on the other hand, in ethyl-alcoholic solution it is the member containing five carbon atoms in the growing chain which has the conspicuous value.

In the series of acetates particularly instructive results have been obtained. Here the grouping $—O\cdot CO\cdot CH_3$ is the smallest of the corresponding groups in the compounds examined, and it is found that the values of $[M]^{20^\circ}$ decrease rapidly in the series until the member $C_6H_{13}\cdot CH(O\cdot CO\cdot CH_3)\cdot CH_3$ is reached, after which the rate of decrease becomes very much smaller. It should, however, be noted that in all the series of esters the growing chain $—CO\cdot R$ is attached only indirectly to the asymmetric carbon atom by means of another oxygen atom.

By including the examination of these esters in the investigation, the authors' original plan has been abandoned, but this is justified as the optical rotatory dispersions of the esters in general offer such a striking contrast to those of the carbinols. Thus for the latter it has been observed that (1) in an homologous series the rotatory dispersion ratio becomes constant (within the limits of experimental error) as soon as the growing chain has become distinctly the largest group attached to the asymmetric carbon atom, and (2) the value of the ratio for a given carbinol is constant between wide temperature limits (20° to 200°), whereas for the esters (except perhaps for some of the β -butyl esters) these generalisations do not hold.

The rotatory powers of the esters as a rule are decreased (often to the extent of changing the optical sign) by solvents and by increase of temperature, the depressing effect for each set of conditions being a similar one for each of the different series. By suitable choice of conditions either of temperature or of concentration in some such solvents as carbon bisulphide, pyridine, or benzene, the esters can be caused to exhibit anomalous rotatory dispersion. These conditions must be such that the $[a]_D$ of the d ester is depressed so that it lies between $+2.5^\circ$ and $\pm 0^\circ$. It has been shown above how in a qualitative sense the relations between the molecular rotatory powers of the esters when measured at 20° in the homogeneous state can be explained, but such explanation would probably have been impossible had the temperature at which the comparisons were made been selected at above 150° when so many of the esters exhibit anomalous dispersion.

The results appear to be due to alterations in the complexity of the molecules and can be co-ordinated on the

assumption that each ester is a mixture of two isomers, which have rotatory powers of opposite sign and different dispersive power. Such co-ordination is effectively brought out by the construction of "characteristic diagrams" drawn in the manner described by Armstrong and Walker (*Proc. Roy. Soc.*, 1913, A, lxxxviii., 388).

The present authors therefore suggest that (1) in general two forms of any one ester can exist; (2) the proportion of these two forms present varies according to the conditions of temperature or solution; (3) the difference is due to the exercise of the supplementary valency of the oxygen atom in one of the forms, and (4) when the two forms differ in dispersive power and optical sign, anomalous dispersion may be observed. In an homologous series of esters the effect of the growing chain on the rotatory powers of the two isomers (supposed to be present) would be likely to vary in a more or less regular manner throughout the series. In the series of esters mentioned above, since the region in which anomalous dispersion has been observed lies near to $\pm 0^\circ$, the dispersive powers of the isomers cannot be very widely different in the case of any of the compounds, whilst if there be any connection at all between chemical constitution and rotatory power the values of the rotatory power of the various esters should bear some relationship, as all the radicles are alike. No numerical relation has so far been observed—it is not yet possible to choose a set of conditions suitable for instituting comparisons—but it is significant that the same characteristic diagram appears to correlate all the determinations of the rotatory power of one of the optical antipodes of the compounds comprising the eleven series mentioned above, in addition to other derivatives of the carbinols themselves.

In this respect the properties of *l*-methyl α -naphthyl carbinol are very instructive. It melts at 47° , but will remain in the supercooled state, and at 10° it has $[\alpha]_{\text{H}_g} -8.0^\circ$, showing at and within a few degrees of this temperature anomalous dispersion; at 120° it has $[\alpha]_{\text{H}_g} -77.4^\circ$, at and above which temperature the dispersion remains approximately constant. In 5 per cent carbon bisulphide solution it has $[\alpha]_{\text{H}_g} -198.9^\circ$, whilst it

forms a dextro-rotatory hydrogen phthalic ester, which in 5 per cent ethyl alcoholic solution has $[\alpha]_{\text{H}_g} +171.7^\circ$.

These determinations range over 370° and can be correlated on one characteristic diagram. It can be assumed here that (1) two forms of the carbinol with different dispersive power and of opposite optical sign exist, owing to different dispositions of the valencies in the naphthyl radicle; and (2) the rotatory powers of these two forms and their esters are principally determined by the groups attached to the asymmetric carbon atom.

At least it seems now capable of proof that the rotatory power of a derivative of a given optically active compound is some function of the rotatory power of the latter, although the highly constitutive character of this physical property makes the problem still one of extreme complexity.

Specific Heats and Heats of Fusion of the Alkaline Metals.—E. Rengade.—The atomic specific heat of the alkaline metals, although always approximately 6, increases regularly with the atomic weight, while the atomic heat of fusion regularly decreases. The ratio of the atomic heat of fusion to the absolute temperature of fusion is a number which is nearly constant for all the four metals investigated; the difference between the extreme numbers (for potassium and caesium) does not exceed 2.5 per cent. If the variation of the specific heats with the temperature is investigated it is found that for the solid metals the temperature coefficient increases rapidly for rubidium and caesium. With the liquid metals the reverse is the case.—*Bull. Soc. Chim. de France*, xv., xvi., No. 4.

THE RELATIVE ABUNDANCE OF SEVERAL METALLIC ELEMENTS.

By F. W. CLARKE and GEORGE STEIGER.

DURING the past twenty-five years several estimates of the relative abundance of the commoner chemical elements have been published from the laboratory of the United States Geological Survey. (For the latest of these estimates see *Bulletins* 419 and 491, U.S. Geol. Survey; also a paper in *Proc. Am. Phil. Soc.*, li., 214). These estimates, however, covered only such constituents of the earth's crust as are usually determined in the course of fairly complete analyses, including, in many cases, the less important elements barium, strontium, nickel, chromium, vanadium, and zirconium. For the more familiar metals, copper, lead, zinc, and arsenic, no really adequate data were available, and no attempt was made to compute either their abundance or their frequency. Such attempts have been made by others, however, but not altogether conclusively. (See, for example, Vogt, *Zeit. Prakt. Geol.*, 1898, pp. 225, 314, 377, 413, and 1899, pp. 10, 274; and Kemp, *Econ. Geol.*, i., 207).

In order to gain a definite idea as to the relative abundance of the elements in question, a number of composite analyses were made. That is, in each group of substances investigated, many samples were blended into one uniform sample, and that was then analysed. The average content of each metal was determined in that way with as close an approximation to accuracy as could have been attained by many individual analyses. Four such composites have been studied thus far; namely, two of oceanic clays, contributed by Sir John Murray (for the complete analyses of these clays see *Journ. Geol.*, xv., 783); one of silt or mud from the delta of the Mississippi; and one of igneous rocks which had previously been analysed in the laboratory of the Survey. For the Mississippi silt the general analysis, not heretofore published, is as follows:—

TABLE I.—Composite Analysis of 235 Samples of Mississippi Silt.

SiO ₂	69.96
Al ₂ O ₃	10.52
Fe ₂ O ₃	3.47
MgO	1.41
CaO	2.17
Na ₂ O	1.51
K ₂ O	2.30
H ₂ O—	3.78
H ₂ O+	1.96
TiO ₂	0.54
ZnO	0.05
CO ₂	1.40
P ₂ O ₅	0.18
SO ₃	0.03
S	0.07
Cl	0.30
F	0.07
Cr ₂ O ₃	0.01
V ₂ O ₃	0.02
NiO	0.017
MnO	0.06
BaO	0.08
SrO	Trace
CuO	0.0043
ZnO	0.0010
As ₂ O ₃	0.0004
PbO	0.0002
Organic	0.66
	100.6229
Less O	0.13
	100.4929

(NOTE.—Except when otherwise stated the analyses given here were made by Mr. Steiger).

The composite was made up of 235 separate samples, collected by E. W. Shaw. For the determination of NiO, CuO, PbO, ZnO, and As₂O₅, 200 grms. of the silt were taken. The presence of organic matter prevented the separate determination of ferrous iron. The chlorine in this analysis is doubtless due to salt from the Gulf of Mexico.

For the four composite analyses above mentioned the data under immediate consideration are as follows:—

A. The "red clay" of the oceanic depths. Composite of 51 samples dredged from the sea bottom and representative of all the great oceans. The larger part of this material was collected by the *Challenger* Expedition. Determinations (by E. C. Sullivan) of CuO, ZnO, PbO, and As₂O₅ made on 150 grm. portions.

B. "Terrigenous clays," from oceanic depths of 140 to 2120 fathoms. Composite of 52 samples, namely, 4 "green muds" and 48 "blue muds," also mainly from the *Challenger* Expedition. Determinations made on 300 grm. portions.

C. Composite of 235 samples of Mississippi silt, as in the foregoing analysis. For the heavy metals 200 grm. portions were taken.

D. Composite of 329 igneous rocks, all American. Determinations on 90 grm. portions.

In the red clay a trace of molybdenum was also detected by Dr. Hillebrand.

TABLE II.—Summary of Data from Composite Analyses.

	A.	B.	C.	D.	Average.
NiO ..	0.0320	0.0630	0.0170	0.00655	0.0295
As ₂ O ₅ ..	0.0010	Trace	0.0004	0.00074	0.0005
PbO ..	0.0073	0.0004	0.0002	0.00081	0.0022
CuO ..	0.0200	0.0160	0.0043	0.01167	0.0130
ZnO ..	0.0052	0.0070	0.0010	0.00638	0.0049

These figures give quite clearly the order of magnitude of the several percentages, and they are corroborated by the work of other investigators. In a series of 36 igneous and metamorphic rocks of British Guiana, Harrison found a mean percentage of 0.025 copper. In 23 of his samples lead was also sought for, and detected in 5 of them, the maximum amount being 0.02 per cent. In a typical specimen of the Columbia River basalt Wells found 0.034 of copper, and the same quantity was determined by Jensen in an andesite from Fiji. In the porphyries of Leadville, Colorado, Hillebrand was able to determine lead. Out of 18 samples, taken at points remote from ore bodies, the average amount found was 0.002 per cent of PbO. One porphyry also yielded 0.008 per cent of zinc oxide, and a rhyolite contained 0.0043 per cent.

In four rocks, granite, porphyry, and diabase from the Archean of Missouri, Robertson determined the following percentages of lead, zinc, and copper:—

Pb	0.00197 to 0.0068 ; average, 0.004
Zn	0.00139 to 0.0176 ; average, 0.009
Cu	0.00240 to 0.0104 ; average, 0.006

The adjacent limestones also carried these metals, but in slightly smaller proportions. Similar results were obtained by Finlayson from igneous rocks adjacent to lead mines in Great Britain. His averages are—Pb 0.0032 per cent, and Zn 0.028. In the lime stones and dolomites of the Dubuque region, Iowa, Weems determined lead and zinc. The average of 9 samples gave 0.00326 per cent of Pb, and 0.00029 of Zn. Many other determinations of the heavy metals in rocks are scattered through the literature of geology, but these examples are sufficient to illustrate what has long been known. The researches of Forchhammer, of Sandberger, and of Dieulaufait are familiar to geologists, but they lack the quantitative basis which is supplied by the composite analyses given here. (For

literature references see *Bulletin* 491 U.S. Geol. Survey; "The Data of Geochemistry," pp. 600—602, 643). The heavy metals are widely diffused throughout the crust of the earth, and generally in determinable proportions. The order of abundance, as now ascertained, appears to be Ni, Cu, Zn, Pb, As, with, of course, local variations.

With the aid of the estimate here given for zinc, which is near 0.005 per cent of ZnO or 0.004 Zn, it becomes possible to gain some notion as to the relative abundance of cadmium; for the two metals are commonly associated. In 10,906 shipments of zinc ores from Webb City and Joplin, Missouri, mostly in carload lots, Waring found an average percentage of 57.96 Zn and 0.358 Cd. (Cited by Siebenthal in U.S. Geol. Survey, "Mineral Resources," 1908, i., 796; see also, for other data, Waring's paper in *Journ. Am. Chem. Soc.*, xxvi., 16). The ratio is 1 Cd to 162 Zn. From 42 analyses of sphalerite given in Hintze's "Handbuch der Mineralogie," the mean ratio is 1 to 163. From 82 analyses of European zinc ores, cited by Jensch, the ratio 1 to 277 appears (Ahren's "Sammlung Chem. Tech. Vorträge," iii., 201). The mean of these three estimates is 1 to 201; that is, in round numbers, zinc seems to be about 200 times as abundant as cadmium. A more precise estimate can hardly be made at present; but the figure is better than no estimate at all. It has a quantitative basis, and is therefore something more than a mere guess. If the percentage of zinc in the earth's crust is 0.004, then that of cadmium is of the order of 0.00002.

In the course of the regular rock analyses made in the laboratory of the Geological Survey, many determinations have been made of elements of minor quantitative importance. These determinations are numerous enough to fix their numerical significance between maximum and minimum limits as follows:—

In round numbers, about 1200 such analyses, nominally complete, have been made, and in 793 of them barium oxide was determined or proved to be absent. The mean of these determinations, counting absences as zero, is 0.104 per cent, which is probably a maximum. If the remaining 407 rocks were all free from barium, and so regarded, the average percentage of BaO would be 0.069, a minimum, and between the two figures the most probable value would lie, their mean being 0.086. Upon this basis of computation the following table of percentages has been constructed:—

TABLE III.—Summary of Data from Rock Analyses.

	Number of determinations.	Maximum.	Minimum.	Mean.
BaO ..	793	0.104	0.069	0.086
SrO ..	649	0.040	0.022	0.031
Li ₂ O ..	581	0.011	0.005	0.008
NiO ..	299	0.026	0.006	0.016
Cr ₂ O ₃ ..	293	0.050	0.012	0.031
V ₂ O ₅ ..	102	0.026	0.002	0.014
ZrO ₂ ..	372	0.023	0.007	0.015

In three of the composite analyses already cited, similar determinations were made, and the results obtained fit in fairly well with the figures of this table.

The percentages found are shown in the following table:—

TABLE IV.—Data from Analyses of Composite Samples.

	Red clay.	Terrigenous clay.	River silt.
BaO ..	0.17	0.05	0.08
SrO ..	0.046	0.025	Trace
NiO ..	0.032	0.065	0.017
Cr ₂ O ₃ ..	0.01	0.04	0.01
V ₂ O ₅ ..	0.028	0.028	0.02
ZrO ₂ ..	Undet.	Undet.	0.05

The data so far obtained may not be final, but they clearly indicate the several orders of magnitude which it was sought to determine.—*Journal of the Washington Academy of Sciences*, iv., No. 3.

A CORRELATION OF THE ELASTIC BEHAVIOUR OF METALS WITH CERTAIN OF THEIR PHYSICAL CONSTANTS.*

By JOHN JOHNSTON.

As is well known, the effect of pressure acting on both the solid and liquid phase of a single substance is to raise or lower its melting-point according as the process of melting is accompanied by an increase or a decrease of volume respectively, the latter being the exceptional case. But when pressure acts only on the solid phase, but not—or not to the same extent—on the liquid phase, the melting-point is always lowered and by an amount which is many times as great as the corresponding change produced by the same pressure acting on both the liquid and the solid phase. For example, the melting-point of ice is lowered by 0.0075° per atmosphere of equal pressure, but by about twelve times as much, or 0.009° per atmosphere, when the pressure acts only on the ice (see Note 1). The latter type of pressure we shall for convenience in what follows designate by the term "unequal pressure."

A study of the work of Spring and others rendered evident a parallelism between the melting-point of a substance and the ease with which it will, when subjected to (non-uniform) compression, flow or weld into a more or less solid block; namely, that the higher the melting-point of the material the less readily does it flow, or weld together, under compression. From this it is obvious that, if it be assumed that the process of flow is a manifestation of a real melting produced by the compression, the pressure must be unequal in character; that is, the pressure acting on the solid must be greater than that on the liquid phase. For, when the same pressure acts on both phases, the melting-point of practically all substances is raised, and not lowered, as, on this explanation of the phenomenon, we assume it to be. It seemed of interest, therefore, to calculate the effect of unequal pressure in lowering the melting-point of metals, to compute the amount of such pressure required to cause the metal to melt at or about the ordinary temperature, and to investigate if the pressure computed in this way can be correlated with any of the mechanical or other properties of the metals.

The equation made use of in calculating the effect of unequal pressure on the melting-point is derived most readily in the way employed by G. N. Lewis (*Journ. Am. Chem. Soc.*, 1908, xxx., 680) in a parallel case—the calculation of the variation of osmotic pressure with temperature (see Note 2).

Let A be the activity of the substance in the solid phase, and A' the activity in the liquid phase (see Note 3). Now, if the pressure on the solid phase alone is increased by dP , then the temperature of equilibrium will be changed by an amount dT . Since both phases are initially in equilibrium, the activity of the solid (A) and that of the liquid (A') must be equal; moreover, they must again be equal when equilibrium is re-established. Hence $A = A'$, and $dA = dA'$, or $d \ln A = d \ln A'$.

Now, the change in $\ln A$ is due to temperature change alone; the change in $\ln A'$ is due to change in temperature and change in pressure; that is—

$$d \ln A = \left(\frac{\partial \ln A}{\partial T} \right) dT$$

and—

$$d \ln A' = \left(\frac{\partial \ln A'}{\partial T} \right) dT + \left(\frac{\partial \ln A'}{\partial P} \right) dP.$$

Equating the right hand members of these equations, we have—

$$\left(\frac{\partial \ln A}{\partial T} \right) dT - \left(\frac{\partial \ln A'}{\partial T} \right) dT = \left(\frac{\partial \ln A'}{\partial P} \right) dP.$$

Substituting for the partial differentials their values from

the fundamental thermodynamic equations (see Note 4), and combining the left hand terms, gives—

$$\frac{LdT}{RT^2} = \frac{VdP}{RT}$$

or—

$$\frac{dT}{dP} = \frac{VT}{L} \dots \dots \dots (I.)$$

where V is the molal volume of the solid phase, T its melting-point on the absolute scale (both phases under the same pressure), and L its molal heat of fusion. The quantities V and T are always positive, but L (as here used) is always negative; hence application of excess pressure on the solid phase always lowers the melting-point (see Note 5).

This differential equation is rigorously correct; but in order to integrate it, we must know how V and L change with the temperature and with the pressure. The variation of V is determined by the coefficients of expansion and of compressibility, which are known for comparatively few substances. With regard to the other factors, our knowledge of L at the ordinary melting-point under atmospheric pressure is as yet extremely unsatisfactory in character and limited in scope, while our ignorance of its variation with either temperature or pressure is practically complete. However, in the case of the metals at least, this difficulty is not so serious, as is shown by the following considerations:—

The variation of melting-point with pressure, acting equally on both phases, for all the metals which have so far been investigated, has been found to be practically linear within the error of experiment (see Note 6). It is a necessary consequence of this linearity that with increasing pressure the relation between L and $(V - V')$ (V' is the molal volume of the liquid phase) must be linear, or, in the limiting case, remain practically constant. It is, therefore, very plausible that we are justified in assuming that the variation of L with V is linear. Integrating Equation I. on this basis, between the limits T_1 (the ordinary melting-point at 1 atm. pressure, expressed on the absolute scale) and a given temperature θ , we obtain the equation—

$$P = \frac{L}{V} \ln \frac{T_1}{\theta} \dots \dots \dots (II.)$$

Instead of the molal values we may substitute the heat of fusion (Q_1) per grm. of substance, and the density (D_1) of the solid, at the ordinary melting-point (T_1) (see Note 7); making the necessary transformations we obtain finally the equation—

$$\phi = 95.1 Q_1 D_1 \log \frac{T_1}{\theta} \dots \dots \dots (III.)$$

which enables us to calculate the melting pressure (ϕ , expressed in atmospheres) corresponding to the temperature θ ; that is, ϕ is the pressure required to cause the substance to melt at the absolute temperature θ .

This formula has been applied to the calculation of the excess pressure (acting on the solid only) required to cause the metal to melt at 27° (that is, $\theta = 300^{\circ}$) in the case of all the metals for which values of Q are given in "Landolt-Börnstein-Meyerhoffer Tabellen" (2 Aufl., p. 470) (see Note 8). For some metals more than one value is given, but it is at present impracticable to determine which are most reliable; for this reason the mean value was adopted in all such cases. For the same reason the general mean value of the density, as given in the tables (p. 224), was taken. The melting points are those now generally adopted.

The data and results are brought together in Table I., in which the metals are arranged in the order of increasing values of the melting pressure calculated in this way from Equation III. It was conjectured that this order might bear some relation to that obtained when these metals are arranged with reference to the relative values of the elastic constants and mechanical properties.

* From the *Journal of the American Chemical Society*, vol. xxxiv., No. 6.

TABLE I.—Lowering of Melting point of Metals Effected by One Atm. Unequal Pressure, together with the Computed Melting Pressures at Ordinary Temperatures.

Metal.	Melting-point.		Heat of fusion. Q.	Density. D.	$\Delta T_1(a)$	$\phi_{27}(b)$
	T_1 .	T_2 .				
K	62	335	15.7	0.87	0.59	64
Na	97	370	31.7	0.98	0.29	266
Pb	327	600	5.4	11.37	0.24	1760
Sn	232	505	14.1	7.29	0.12	2200
Bi	270	543	12.5	9.80	0.11	3000
Cd	321	594	13.7	8.64	0.12	3300
Al	658	931	42.0	2.60	0.21	5100
Zn	419	692	28.0	7.1	0.084	6900
Ag	960	1233	23.0	10.50	0.12	14000
Cu	1083	1356	43.0	8.93	0.086	24000
Pd	1550	1823	36.3	11.4	0.11	31000
Pt	1755	2028	26.2	21.5	0.084	46000

(a) This column, which represents the melting-point depression produced by 1 atm. excess pressure acting on the solid, is added merely to give an idea of the magnitude of this quantity. The values given are calculated from the formula $\Delta T_1 = T_{141.30} Q D$ which is easily derived from Equation I.

(b) It should be observed that the values of ϕ given in the preliminary note (*Journ. Washington Acad. Sci.*, 1911, i., 260) were calculated by a formula which holds strictly only so long as ϕ , or the difference between T and θ , is small. The more accurate mode of calculation from Equation III. of the present paper leads to somewhat higher numerical values of ϕ , but does not alter the order of the ϕ values; so that this change does not affect the argument.

The most obvious mechanical property with which to compare the series of ϕ values is the flow pressure (see Note 9). This was determined for a series of metals by Tammann, Verigin, and Levkojeff (*Ann. Phys.*, 1903, x., 649); later, and independently, by Kurnakof and Zhemchuzhny (*Zeit. Anorg. Chem.*, 1909, lxiv., 174). Arranged in the order of decreasing ease of flow, the metals follow in the order K, Na, Pb, Tl, Sn, Bi, Cd, Zn, Sb, a sequence which is identical with that deduced thermodynamically and presented in Table I. But not only is the sequence of ϕ values identical with that of the low pressure; it is practically identical with the sequence obtained when the metals are arranged in the order of any of their elastic properties for which measurements have been made. This is shown by Table II., in which have been brought together all the data available on the elastic properties, namely, compressibility, hardness, tensile strength, elastic limit, elastic modulus, and modulus of rigidity.

From Table II. it is evident that, as the value of ϕ increases, the compressibility decreases, and the values of the other elastic properties increase steadily. The exceptions to this statement are very few as regards any one property, and vary irregularly as we pass from one property to another; in other words, there are no systematic divergences between the sequence of the metals as derived from the thermodynamic relationship discussed in this paper and that obtained when they are arranged progressively with reference to any one of their elastic properties. The slight divergences are no greater than one might expect from the uncertain character of the thermal data, on the one hand, and of the elastic constants on the other. Indeed, excellent agreement could have been obtained by selecting for each metal an appropriate value from the somewhat discordant data for the elastic constants in the Landolt-Börnstein-Meyerhoffer Tabellen; but it was deemed more commendable to take a general mean of all the values there given, as it was impracticable to determine just which values represent most accurately the true elastic constants of the various metals.

The purely elastic properties of metals have often been

collated and compared, and it has been surmised repeatedly that these properties are some function of the melting-point of the metal (see Note 10). But, so far as the writer is aware, no one has advanced further than a statement of the general parallelism between elastic properties and melting-point—a statement to which there are some notable exceptions, lead, aluminium (see Table II.), also a large number of alloys, which seriously limited its scope and usefulness. When arranged with reference to the function of the melting-point deduced in this paper, the above two metals cease to be exceptions (see Note 11).

One other piece of presumptive evidence in favour of this point of view may also be mentioned, namely, a comparison of the values of ϕ with the flow pressures of tin as determined by E. Jänecke at a series of temperatures (*Metallurgie*, 1911, viii., 68). In default of knowledge of the variation of Q with temperature and pressure, we may justifiably consider Q and D as constants. For any one metal therefore Equation III. may be written, since T_1 is also constant,—

$$\phi = K_1 - K_2 \log \theta \quad \dots \quad (IV.),$$

where K_1 and K_2 are constants, the values of which depend upon Q , D , and T_1 . The graph of Equation IV., which gives the variation of ϕ with θ , is very similar to the curve plotted from Jänecke's results; with increasing temperature both diminish at about the same decreasing rate.

From the above, then, it appears to be true that the mechanical properties of metals are correlated with the amount of pressure—assumed to act on the solid alone—requisite to cause the metal to melt at or near the ordinary temperature. This pressure in turn depends upon the melting-point, the density, and the heat of melting of the metal. The first two of these quantities are known to be periodic functions of the atomic weight, and there is every reason to believe that the heat of melting, and therefore also ϕ , is. Therefore, reasoning from the observed parallelism, we should expect some, or all, of the elastic properties to be periodic functions. So far, thorough measurements have been made only on the compressibility, which, according to Richards, shows marked periodicity.

The remarkable concordance shown in Table II., which can hardly be due to coincidence, suggests that the "flow" of metals—or, indeed, every permanent distortion of a crystalline solid—is due to an actual fusion (with subsequent re-solidification) of the crystals. The validity of this view is supported by a large number of well-known facts, e.g., that a metal requires progressively less effort to cause it to weld—or to forge it—the higher its temperature. Moreover, it is corroborated by a large number of observations, which demonstrate the existence of important differences between metal which has "flowed" or has been subjected to deformation of any kind and the same metal in the annealed condition.

All the available evidence (see Note 12) goes to show that there is:—(a) A difference in the energy content of the strained and unstrained metal, which is manifested in a difference between the two forms—(1) in their electrolytic potential when immersed in a solution, (2) in their thermo-electric power, (3) in their heat of solution; (b) a difference in structure manifested in differences in—(1) microscopic appearance, (2) mechanical properties—hardness, tensile strength, &c., (3) density (see Note 13), (4) conductivity for heat or electricity, &c. For any one metal these differences vanish about a single temperature common to all—thus for silver at about 260°—that is, at the temperature which annealing proceeds with appreciable rapidity.

Notes.

1. Cf., J. H. Poynting, *Phil. Mag.*, 1881, [5], xii., 32; Ostwald's "Lehrbuch der Allgemeinen Chemie," 2 Aufl., vol. ii., II., p. 374; or Roozeboom's "Heterogend Gleichgewichte," vol. i., p. 213.

2. I am much indebted to Prof. Lewis for bringing to my attention this method, which is so much more succinct

TABLE II.—Relative Values of the Elastic Constants of Metals (see Note).

Metals in order as in Table I.	Compressibility. (a).	Hardness. (b).	Tensile strength.		Elastic limit.			Elastic (Young's) modulus. (g).	Rigidity modulus.	
			(c).	(d).	(e).	Lower. (f).	Upper. (f).		(h).	(i).
K	31.5	0.5	—	—	—	—	—	—	—	—
Na	15.4	0.4	—	—	—	—	—	—	—	—
Pb	2.2	1.5	2.0	21	0.3	25	102	17	5	0.80
Sn	1.7	1.8	2.1	36	4	34	55	34	16	1.50
Bi	2.8	2.5	—	—	—	—	—	32	12	—
Cd	1.9	2.0	—	48	—	28	109	71	17	2.31
Al	1.3	2.9	—	—	—	283	600	70	29	2.55
Zn	1.5	2.5	13	—	10	125	770	78	31	—
Ag	0.84	2.7	22	272	12	—	—	70	39	2.67
Cu	0.54	3.0	25	316	12	203	2780	108	42	4.37
Pd	0.38	4.8	—	—	27	—	—	103	46	—
Pt	0.21	4.3	29	—	26	—	—	161	52	6.46

NOTE.—It is to be noted that the values given in the table are relatively only, and are not always expressed in the same units (e.g., columns c and d, e and f, h and i):—

- (a) As given by Richards and collaborators (*Journ. Am. Chem. Soc.*, 1909, xxxi., 156)
 (b) According to Rydberg ("L.-B.-M. Tabellen," p. 57).
 (c) "L.-B.-M. Tabellen," p. 53).
 (d) Wertheim (1848) quoted by Faust and Tammann (*Zeit. Phys. Chem.*, 1911, lxxv., 118).

- (e) "L.-B.-M. Tabellen," p. 53.
 (f) As determined by Faust and Tammann (*loc. cit.*).
 (g) and (h) General mean of the (sometimes very discordant) values given in "L.-B.-M. Tabellen," p. 43.
 (i) Horton (*Trans. Roy. Soc., A*, 1905, cciv.).

than the mode of derivation which I had at first made use of.

3. For a definition and discussion of the term "activity," see Lewis, "Outlines of a New System of Thermodynamic Chemistry," *Proc. Am. Acad.*, 1907, xliii., 259; *Zeit. Phys. Chem.*, 1907, lxi., 129.

4. Lewis, Equations V. and VIII., *Proc. Am. Acad.*, 1907, xliii., 266; *Zeit. Phys. Chem.*, 1908, lxi., 137.

5. This lowering is, of course, relative to the melting-point when that pressure which now acts on the liquid alone (the solid being subject to pressure in excess of this) acts on both solid and liquid. In other terms, if the melting-point is denoted by T with subscripts and superscripts to represent the pressure acting on the solid phase and liquid phase respectively, then $T_{P+\Delta P}^P$ is always lower than T_P^P , the magnitude of this lowering being dependent on the excess of pressure ΔP acting on the solid. Now T_P^P may be higher or lower than T_1^1 (the ordinary melting-point at atmospheric pressure), according as the volume change on melting is positive or negative; consequently, in some cases $T_{P+\Delta P}^P$ may be higher than T_1^1 , but this will be so only when ΔP is small compared to P, a contingency which, we believe, does not affect the main considerations advanced in this paper.

6. Tammann, *Zeit. Anorg. Chem.*, 1904, xl., 54, with K and Na; Johnson and Adams, *Am. Journ. Sci.*, 1911, xxxi., 501; *Zeit. Anorg. Chem.*, 1911, lxxii., 11, with Sn, Bi, Cd, Pb at pressures up to 2000 atm.; Bridgman, *Proc. Am. Acad.*, 1911, xlvii., 347, with Hg up to still higher pressures.

7. In the computations which follow, the value of the density at the ordinary temperature was used. This was done because of the uncertainty in the appropriate correction; moreover, our present knowledge of D at the ordinary temperature is so unsatisfactory that it would be altogether futile to apply any such correction, especially as the accuracy of the present values of Q is so doubtful.

8. Excepting iron, on account of the uncertainty of what "iron" is, and the disparity of the recorded values. The value given for nickel in "Landolt Börnstein-Meyerhoffer Tabellen" (p. 470) as a heat of fusion (taken from Pionchon, *Ann. Chim. Phys.*, 1887, [6], xi., 106) was found, on reference to the original, to be a heat of transformation (occurring somewhere between 230° and 400°); consequently nickel could not be included. Similarly, Pionchon's values for iron given in "L.-B.-M." (p. 470) are heats of transformation). Mercury and gallium are omitted, since

they are liquid at ordinary temperatures. The value of Q for aluminium is somewhat doubtful; it was calculated from the "total heat" (as given in "L.-B.-M.") by means of the specific heat of aluminium (0.30) as given by Bontschew ("L.-B.-M.," p. 383). No alloys could be included owing to lack of the necessary data; in any case, the formula is applicable only to those alloys which melt completely at a definite temperature.

9. The amount of compression required to cause a material to flow is characteristic of the material under specified conditions; but at constant temperature it varies, as is obvious, with the size of the aperture through which the flow takes place; probably also it depends upon the shape of the aperture and upon other subsidiary factors. Hence determinations of flow pressures are comparable only when they have all been made in the same apparatus and in the same way. This condition is fulfilled by the experimental observations cited, which lead to reliable relative values of the flow pressure for a series of metals.

10. No references are given to this, because the author found it impracticable to examine all of the voluminous literature in order to determine with whom each particular suggestion originated. Some of the points are discussed by Kurnakov and Zhemchuzhny (*Zeit. Anorg. Chem.*, 1908, lx., 1; 1909, lxiv., 149).

11. The Formula III. could not be applied to alloys owing to lack of the necessary data. In any case the formula is applicable presumably only to such alloys as melt completely at a constant and definite temperature.

12. Cf. G. T. Beilby (*Phil. Mag.*, 1904, [6], viii., 258—276), who discusses the evidence in detail.

13. Kahlbaum, Roth, and Siedler (*Zeit. Anorg. Chem.*, 1902, xxix., 197); Kahlbaum and Sturm (*Zeit. Anorg. Chem.*, 1905, xli., 217); Spring (*Journ. Chim. Phys.*, 1903, l., 593; *Rec. Trav. Chim.*, 1904, xxiii., 1). This subject is fully discussed by Johnson and Adams (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 563).

(To be continued).

Catalytic Action of Kaolin on the Combination of Hydrogen and Oxygen.—Jacques Joannis.—The presence of kaolin induces the combination of H₂ and O₂ at temperatures at which it does not take place in glass, viz., at 230° and above. In the conditions investigated by the author the amount of water formed is proportional to the duration of contact. The activity of the kaolin diminishes as the temperature to which it has previously been heated is raised.—*Comptes Rendus*, clviii., No. 7.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

CURIOUS ANOMALY OF HYDROGEN.

It is known that one of the most surprising properties of wood charcoal is that which it possesses of absorbing gases with so much energy when it is cooled to the temperature of liquefied air that, in a single moment, with its help, one can make in an enclosed space that curious vacuum—impermeable even to an electric charge—that is named the Vacuum of Hittorf. Up till now it was thought that this property was joined to the respective aptitude of different gases to liquefaction, so that hydrogen, very refractory to liquefaction, could not be much absorbed. However, M. George Claude having applied this property to the formation of his neon tubes, has seen, to his great satisfaction, that the hydrogen given off by the electrodes is rapidly eliminated, whereas the neon subsists. M. Claude next undertook some direct measures, which have shown him that, effectively, hydrogen is the most curious exception to the rule deduced from the aptitudes to liquefaction, since instead of being less absorbed than neon, it is absorbed something like a hundred times more! So then, in these very especial conditions of temperature which exclude the hypothesis of a chemical action, we discover this curious tendency of hydrogen to become absorbed in the metals cobalt, palladium, and platinum, which constitutes one of the most interesting points of its history, and which must probably be sought for, no more in a chemical action, but doubtlessly far rather in the form or the mass of the atom of hydrogen.

ESTIMATION OF TRACES OF ARSENIC.

MM. Moreau and Vinet have been led by their former works on the employment of arsenical products as insecticides for the vine, to take notice of the consequences of this employment from a hygienic point of view, and further to study the estimation of very small quantities of arsenic. Their method of estimation consists in causing the arseniated hydrogen, supplied by the matters to be analysed, to act on a solution of silver nitrate. In suitable conditions, completely precised by authors, there is formed a precipitate of silver that affects the form of a ring, the importance of which, by comparison with rings used as types, permits of the appreciation of the amount of arsenic to be determined. The method is remarkably simple and enables the recognition of one thousandth of a mgrm. of arsenic.

LAKES OF SODA.

Quite recently some English engineers, who were constructing the Ongonda railway, discovered the soda lake of Magadi in British East Africa. This bed is absolutely unique of its kind, not only by its extent, but by the very remarkable purity of the soda it contains. M. S. Kestner has just given to the French Société des Ingénieurs Civils some interesting information on this natural curiosity. This African lake seems to contain at least 200 millions of tons of carbonate of soda, almost entirely pure. Already, in Egypt, the lakes of Wadi-Natron were known. These latter contain natural deposits of carbonate of soda, but which is much less pure and more difficult to exploit than that of Lake Magadi. According to M. Kestner it is the residues—accumulated during thousands of years—from the concentration of river or spring water running into these lakes, that form basins with no issue, which have been the cause of these deposits. The waters, entirely evaporated, have left behind them, in the lakes of Wadi-Natron and Magadi, all the salts they contained, and generally the carbonate of soda is accompanied by sulphate and chloride. Exceptionally, in the Lake Magadi, only the carbonate of soda is present. M. Kestner thinks, also, that other known beds may be put into exploitation before long, and that it is very likely that other large deposits of this salt may be

discovered, probably in more accessible regions and at a cheaper cost than in equatorial Africa. In these conditions is it not possible that the soda industry may eventually disappear in the face of this competition of the natural product?

CHEMICAL SOCIETY.

Ordinary Meeting, March 19, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President,
in the Chair.

REFERENCE was made to the loss sustained by the Society through the death of Daniel Bain (Gateshead), Harry Burrows (Southgate), Robert Kennedy Duncan (Pittsburg), Leonard Clifford Green (Brisbane), Christopher Clarke Hutchinson (Kensington), Joseph William Thomas (Shortlands), and Francis Vacher (Birkenhead).

Messrs. A. P. L. Blaxter and A. Bicknell were formally admitted Fellows of the Chemical Society.

The PRESIDENT announced that Prof. Arrhenius has accepted the invitation of the Council to deliver the Faraday Lecture this year. The lecture, entitled "Electrolytic Dissociation," will be delivered in the Theatre of the Royal Institution (by the courtesy of the Managers) on Monday, May 25, at 6 p.m., and further particulars will be announced later.

Certificates were read for the first time in favour of Messrs. Charles Frank Armstrong, Marhourah Sugar Works, Marhourah, B. and N.W. Railway, Saram, Behar, India; Frederick Stanley Baxter, 119, Albert Street, Regent's Park, N.W.; Robert Odell Bishop, 1, Augustine Road, West Kensington, W.; Hugh Miller Galt, B.Sc., M.B., Elm Croft, Withdean, Brighton; Trevor Edward Hodges, 43, Stapleton Hall Road, Stroud Green, N.; William Whalley Myddleton, M.Sc., 6, Fairfield Road, Latchford Without, Warrington.

A Certificate has been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Mr. Birendranath Maitra, 10, Kalighat Road, Bhowanipur, Calcutta, India.

Of the following papers, those marked * were read:—

*77. "The Ignition of some Gaseous Mixtures by the Electric Discharge." By HUBERT FRANK COWARD, CHARLES COOPER, and JULIUS JACOBS.

The pressure of an explosive gaseous mixture may be reduced until ignition becomes impossible with the particular igniting arrangement in use. Such limiting pressures vary considerably with the strength of the igniting electric discharge (see Coward, Cooper, and Warburton, *Trans.*, 1912, ci., 2278, on the ignition of electrolytic gas), but comparable results for various mixtures are obtainable by preserving a constant igniting arrangement of induction coil, cells, spark-gap, &c. The ignition of an explosive mixture the composition of which does not approach too near to the dilution-limit of inflammability proves to be determined chiefly by (1) the energy effect of the discharge itself, a function of the composition and pressure of the mixture; (2) the thermal conductivity of the mixture; and probably (3) an activation of the oxygen. The ignition of such a mixture is therefore a question of strength of spark, and maintained concentration of its energy until the end of the pre-flame period, rather than of the thermal effect of combustion in the path of the spark. Once a true flame is initiated in a homogeneous explosive mixture, its propagation is assured, except in very narrow vessels.

These considerations serve to explain some curious experimental results, of which the following may be quoted:—A series of hydrogen-oxygen mixtures showed a rapidly falling ignition-pressure with increase in oxygen-content until with 60 to 85 per cent of oxygen the ignition-pressure became almost constant. In one apparatus, electrolytic gas at 80 mm. pressure could be inflamed after

the addition of (a) 23 mm. of electrolytic gas itself, or (b) 8 mm. of oxygen or more up to at least 720 mm., or (c) 90 mm. of hydrogen or more up to 210 mm.

Similarly, electrolytic gas much below its ignition-pressure has been ignited after the addition of suitable amounts of nitrogen, carbon dioxide, and even argon.

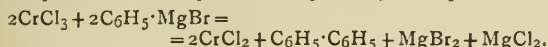
The cyanogen—oxygen, methane—oxygen, and ethylene—oxygen series of mixtures have been examined; also the carbon-monoxide—oxygen series, alone and with various diluents. The carbon monoxide experiments provided the chief evidence respecting the activation of oxygen in the discharge.

*78. "Hydrazoximes of Methyl- and Phenyl-glyoxals." By BIRAN BIHARI DEV.

The hydrazoximes of methylglyoxal, phenylglyoxal, and isonitrosomethylglyoxal, and their benzylidene, benzoyl, and acetyl derivatives, as well as their corresponding azines, have been prepared. The semicarbazones and phenylcarbamyldiazones of isonitroso-acetone, -aceto-phenone, &c., were also described.

*79. "The Action of Chromic Chloride on the Grignard Reagent." By GEORGE MACDONALD BENNETT and EUSTACE EBENEZER TURNER.

It has been shown that when anhydrous chromic chloride is brought into contact with an ethereal solution of magnesium phenyl bromide, chromous chloride and diphenyl are produced in the quantities required by the equation—



No organo-metallic derivatives of chromium could be isolated.

Besides diphenyl, very satisfactory yields of dibenzyl, 4:4'-dimethyldiphenyl, and $\alpha\alpha$ -dinaphthyl have been obtained by similar reactions. A reaction of the same kind was obtained using magnesium isoamyl iodide, but the yield of di-isoamyl was much less satisfactory.

*80. "The Influence of Solvents on Molecular Weights. Part I. Salts." By WILLIAM ERNEST STEPHEN TURNER and CORNELIUS THEODORE POLLARD.

Before any valid interpretation can be drawn of the results of molecular-weight measurements in solution, it is essential that the influence of the medium should be understood. This influence may be physical or chemical, and it is obvious that if the effect of the solvent can be expressed by some physical rule, the interpretation of results is much simplified.

From an examination of existing data, the view had been expressed (Turner, *Trans.*, 1911, xcix., 880) that the main factor influencing the value of the molecular weights of salts in solution is the dielectric character of the solvent, and in order to test how far this view was valid, a systematic review of the subject was undertaken, experiments being made for the purpose on chlorides, bromides, iodides, and a nitrate of organic ammonium bases, dissolved in fourteen solvents. To the new data obtained were added those previously obtained by one of the authors (Turner, *loc. cit.*, and *Trans.*, 1912, ci., 1923), and by other workers, bringing up the total to twenty-three solvents. The following conclusions were drawn:—

1. The molecular weight of an electrolyte is, in a general way, a function or the dielectric character of the solvent, and the statement (Turner, *loc. cit.*) that electrolytic dissociation and molecular association are complementary phenomena, the former appearing in solvents of high, the latter in those of low, dielectric constant, is amply confirmed.

p-Toluidine, of low dielectric constant, is exceptional, but the low results found in this solvent with most of the substances dissolved may be due to combination. Nitrobenzene, in which certain organic substances are strongly associated, falls into line as a solvent for iodides and nitrates, producing apparent dissociation in accordance with its high dielectric constant.

2. Whilst no sharp line can be drawn, association of a

salt occurs, in moderately dilute solutions, when the dielectric constant of the solvent falls below 18, but the extent of association depends both on the solvent and the solute.

3. For solvents of low dielectric constant, the degree of association is not strictly parallel to the dielectric constant.

4. As a general rule, the degree of association of similarly constituted salts falls in the order iodide > bromide > chloride, both in associating and dissociating solvents, thereby affording further evidence of the complementary character of association and dissociation.

Chlorides, in some cases, behave exceptionally.

5. Rise of temperature has a marked influence in decreasing the degree of association of salts.

6. The common view that associated substances dissolved in associated solvents become thereby dissociated is disproved in the case of salts. Such simplification only occurs when the associated solvent possesses a high dielectric constant.

81. "Deliquescence. Part I. The Deliquescence of Salts of Ammonium Bases." By CYRIL JAMES PEDDLE.

Little or no previous systematic study of deliquescence appears to have been made, descriptions of the deliquescence of substances being either the result of visual tests or of exposing a known weight of material on a watch glass or other vessel. Both methods are crude, and have been proved by experience to be deceptive.

The chief factors influencing deliquescence are the temperature and humidity of the atmosphere, the area and depth of the substance used, and the size of the particles of the exposed material. In order to obtain accurate values all these factors must be allowed for, especial care being taken to ensure the air being constantly saturated with moisture.

The amount of water absorbed by 1 grm. of substance is termed the deliquescence of that substance, and results have been obtained accordingly. In addition, the number of grm.-molecules of water absorbed by 1 grm.-molecule of salt was calculated, this value being termed the molecular deliquescence. Some evidence of the rate of absorption was obtained from the ratio—

$$\frac{\text{Molecular deliquescence}}{\text{Time of exposure.}}$$

Amongst homologous compounds, additive properties are absent, the phenomenon of deliquescence appearing to be only constitutive. Solubility is also related to deliquescence, although the relation is a complicated one, being most marked in the case of chlorides.

In general, the order of deliquescence in a series falls with increase in molecular weight, and in the case of corresponding haloid salts the chloride is most deliquescent and the iodide least. The introduction of aromatic radicles brings about a large decrease in deliquescence, whilst salts containing only aromatic radicles are non-deliquescent.

Many of the salts examined had a deliquescence comparable with that of common inorganic drying agents.

82. "Some Derivatives of as-Dipropyl- and Diamyl-oxamic Acids." By HARFORD MONTGOMERY ATKINSON.

Dipropylamine and diamylamine easily react with ethyl oxalate, forming the esters of dipropyl- and diamyl-oxamic acids. The following derivatives were described:—

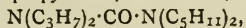
Ethyl dipropylloxamate, $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{N}(\text{C}_3\text{H}_7)_2$, b. p. $143^\circ/10$ mm., which, by the action of ammonia, gives as-dipropylloxamide, $\text{NH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{N}(\text{C}_3\text{H}_7)_2$, m. p. $96-97^\circ$.

as-Dipropylloxamionitrile, $\text{CN}\cdot\text{CO}\cdot\text{N}(\text{C}_3\text{H}_7)_2$, b. p. $120^\circ/14$ mm., which, when treated with hydrogen sulphide, yields as-dipropylthiooxamide, $\text{NH}_2\cdot\text{CS}\cdot\text{CO}\cdot\text{N}(\text{C}_3\text{H}_7)_2$, m. p. $129-130^\circ$.

Thiopiperidylglyoxylamide, $\text{NH}_2\cdot\text{CS}\cdot\text{CO}\cdot\text{NC}_6\text{H}_{10}$, crystals, m. p. $66-67^\circ$; thio-as-diethylloxamide, $\text{NH}_2\cdot\text{CS}\cdot\text{CO}\cdot\text{NEt}_2$, m. p. $126-127^\circ$; thio-as-dimethylloxamide, m. p. $120-121^\circ$.

Dipropylloxamic acid, $\text{CO}_2\text{H}\cdot\text{CO}\cdot\text{N}(\text{C}_3\text{H}_7)_2$, m. p. $73-74^\circ$, and its chloride, $\text{COCl}\cdot\text{CO}\cdot\text{N}(\text{C}_3\text{H}_7)_2$, b. p. $112-116^\circ/14$ mm., which, with dipropylamine, gives tetrapropyl-

oxamide, $[\text{CO}\cdot\text{N}(\text{C}_3\text{H}_7)_2]_2$, m. p. 38–39°, and by the action of heat furnishes *dipropylcarbonyl chloride*, $\text{COCl}\cdot\text{N}(\text{C}_3\text{H}_7)_2$, b. p. 118–120°/21 mm.; *piperidine-1-carboxyldipropylamide*, $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CO}\cdot\text{N}(\text{C}_3\text{H}_7)_2$, b. p. 173°/10 mm.; *dipropyldiamylcarbamide*,—



b. p. 185°/12 mm.; *dipropylformamide*, $\text{HCO}\cdot\text{N}(\text{C}_3\text{H}_7)_2$, b. p. 102°/17 mm.; *ethyl diamyloxamate*, $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{N}(\text{C}_5\text{H}_{11})_2$, b. p. 166–167°/10 mm.; as *diamyloxamide*, $\text{NH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{N}(\text{C}_5\text{H}_{11})_2$, m. p. 182°; *diamylformamide*, $\text{HCO}\cdot\text{N}(\text{C}_5\text{H}_{11})_2$, b. p. 141–145°/18 mm.; *diamylcarbonyl chloride*, $\text{COCl}\cdot\text{N}(\text{C}_5\text{H}_{11})_2$, b. p. 147–149°/14 mm.; and *phenyldiamylcarbamide*, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CO}\cdot\text{N}(\text{C}_5\text{H}_{11})_2$, m. p. 204°.

(To be continued).

INSTITUTE OF CHEMISTRY.

MR. WILLIAM MACNAB delivered his second lecture on "Explosives" at King's College, on Thursday, March 26, 1914.

After referring to the restrictions and regulations imposed on the industry by the Home Office in the interests of safety, the lecturer gave a description of the manufacture of explosives, more particularly nitro-cellulose and nitro-glycerine. Thomson's Displacement process for making gun-cotton is the most important improvement which has been made in this branch, and it has the great merit of producing better gun-cotton at less cost than the old processes, and at the same time of being much less unpleasant and dangerous to the workpeople.

Nathan and Rintoul's Nitratro-Separator for making nitro-glycerine was illustrated and described. Here again progress was in the direction of simplicity and safety, one of the features being the abolition of all cocks in the pipes through which the nitro-glycerine has to pass. The charge of glycerine which can be nitrated in one operation has now increased to 1400 lbs.

The uniformity and excellence with which the manufacture of cordite can be carried out is shown in the small margin in velocities and pressures allowed by the Government.

In the new 15-in. gun the charge of cordite is about 420 lbs., and with a muzzle velocity of 2500 ft. seconds, the variation allowed is only ± 15 ft. seconds.

Referring to the ammonium nitrate class of explosives which consist chiefly of two or three non-explosive ingredients mixed together, the lecturer considered it a distinct hardship and contrary to the public interest that such explosives should be penalised by having to be manufactured under the same expensive conditions as their much more dangerous rivals. They should be allowed to compete on the market with the advantage of their inherent properties.

The test for "permitted" explosives was gone into, its object being to prevent explosions of gas or dust in coal mines from the use of explosives.

The filling charge for shells most generally used in the principal countries is now trinitrotoluol, which is a safe and powerful explosive. Tetranitroaniline is the strongest solid explosive body and is also very stable, and would appear to offer many advantages for torpedoes, military blasting work, and possibly as a charge for shells and aeroplane bombs.

A more pleasing use for explosives has arisen in connection with agriculture. America and the colonies have been the chief fields for this development, but the planting of trees and rejuvenating of existing orchards by means of explosives would appear to be worthy of careful study and trial in this country.

The effect of exploding a cartridge judiciously placed in the ground is to shake it up and fissure it to a far greater extent than can possibly be done by spade work, and new trees planted in such prepared ground make much more

rapid and vigorous growth and bear better, while in an old orchard the ground can be similarly opened and shaken without injury to the standing trees, which, having less dense soil to penetrate with the roots, make corresponding good growth and get a new lease of life. Finally, it was pointed out that chemistry is the foundation of the explosive industry, and that the chemist should play the leading technical rôle in it. A high standard of conduct and conscientious carrying out of work are necessary, seeing that carelessness or a mistake may endanger or sacrifice the lives of many people.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 7, February 16, 1914.

Researches on Acid Salts of Dibasic Acids. *d*-Metallic Camphorates.—E. Jungfleisch and Ph. Landrieu.—The authors have prepared the camphorates of sodium, lithium, ammonium, barium, strontium, calcium, magnesium, manganese, cobalt, piperidine. The investigation of these compounds shows that the neutral or dimetallic camphorates are very stable in presence of water, which does not dissociate them. The acid camphorates are unstable towards water, and are all split up into free acid and neutral dimetallic salt. This indicates that the acid camphorates are the result of the union of camphoric acid with the dimetallic salt; *i.e.*, that they are compounds analogous to the acid salts of monobasic acids.

Constitution of Gaseous and Liquid Chlorides of Cyanogen.—V. Grignard and G. Bellet.—When organo-magnesium compounds act on the halogen derivatives of cyanogen two different reactions may occur:—(i.). Cyanogen iodide gives only the iodine derivative of the organic radical. (ii.). Gaseous cyanogen chloride, on the contrary, gives, with fatty or aromatic magnesium compounds, very little of the chlorine derivative but chiefly the nitrile. With the bromide of cyclo-hexyl magnesium, however, it behaves in exactly the opposite way, giving chlorocyclohexane and very little nitrile. Apparently the gaseous chloride in the free state has the carbylamine structure, but is tautomerised by organo-magnesium compounds, the fatty and aromatic compounds effecting the transformation very rapidly and completely. The liquid chloride is probably the chloroformic nitrile.

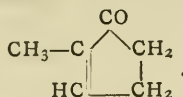
Some Double Chromates.—M. Barre.—Two double chromates of calcium and potassium exist. Both are easily decomposed by water. The chromate formed below 45° has the formula $\text{CrO}_4\text{K}_2\cdot\text{CrO}_4\text{Ca}\cdot 2\text{H}_2\text{O}$. If this is kept at 60° in presence of a solution of CrO_4K_2 the second salt, $\text{CrO}_4\text{Ca}\cdot\text{CrO}_4\text{K}_2$, is formed. Strontium chromate gives only one double salt, *viz.*, $\text{CrO}_4\text{Sr}\cdot\text{CrO}_4\text{K}_2$, and barium chromate behaves similarly. Lead chromate also gives $\text{CrO}_4\text{Pb}\cdot\text{K}_2\text{CrO}_4$. This salt is decomposed by water, but its decomposability diminishes as the temperature rises.

Heat of Formation of Manganese Sulphide.—S. Wologdine and B. Penkiewitch.—The authors have determined the heat of formation of manganese sulphide by observing the heat disengaged by the direct union of finely powdered Mn and S. The numbers obtained are always higher than that of J. Thomsen, who gave -44.390 cal. for the hydrated sulphide. From the authors' experiments the heat of formation of the sulphide from metallic manganese and octahedral sulphur is probably 62.901 cal. per molecule.

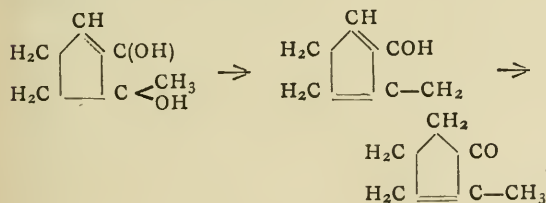
Preparation of Metaphosphate of Molybdenum Sesquioxide.—A. Colani.—Metaphosphate of molybdenum sesquioxide, $3P_2O_5 \cdot Mo_2O_3$, can be prepared by reducing molybdic acid dissolved in metaphosphoric acid by hydrogen at a dull red heat, or by heating anhydrous MoS_2 with orthophosphoric acid in a current of carbon dioxide. The same phosphate may be obtained by reducing at a red heat in a current of CO_2 molybdic acid dissolved in metaphosphoric acid by an excess of molybdenum sulphide. Red phosphorus can also be employed as reducing agent. Molybdenum metaphosphate is stable in dry air; when heated it is oxidised only superficially. In a sealed tube in absence of air it is attacked by water at $250-300^\circ$, phosphoric acid being liberated and a small quantity of hydrogen. It is soluble in a sealed tube at 200° in sulphuric solutions of potassium bichromate or iodic acid. It is not attacked by HCl , HNO_3 , or H_2SO_4 at 100° , but H_2SO_4 acts upon it at its boiling-point, SO_2 being given off.

Syntheses by means of Mixed Organometallic Derivatives of Zinc. 1.4-Acyclic Diketones.—E. E. Blaise.—Of the 1.4-acyclic diketones only one is known, viz., acetylacetone. Others can be prepared by first getting the succinic ether of an acid alcohol, and then the acid dichloride, which is condensed with the organo-zinc compound. Finally, the bicyclo-acetal formed is subjected to alcoholysis by means of methyl alcohol containing a little hydrochloric acid. In general oxyisobutyric acid gives the best results, and a good yield of symmetrical dipropionyl ethane can be obtained from it.

Synthesis of Methylcyclopentenone.—Marcel Godchot.—In 1894 Looff isolated from wood-tar an unsaturated cyclic ketone to which he ascribed the formula—



The author has now confirmed this formula by the following synthesis:—Starting from 1.2-cyclopentane dione by Grignard's reaction he obtained the glycol 1-methyl 2-cyclopentene-1.2-diol. When this glycol is heated to 100° for three hours in presence of oxalic acid and water it is dehydrated and the ketone obtained is identical with the above ketone. The reaction is—

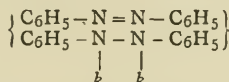


Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvii., No. 3, 1914.

Nitrogen Luminescence.—A. Koenig and E. Elöd.—It has been shown that luminescence in nitrogen after the passage of electric discharges appears equally strongly, even after purification of the gas from traces of oxygen, provided that the gas is free from metallic vapour. If the latter is present the luminescence is very much weakened or altogether prevented. If oxygen, as well as metal, is present the luminescence is increased, the metal being oxidised. An excess of oxygen, however, diminishes the luminescence. All these phenomena are compatible with the assumption that the nitrogen is made active.

Addition of Metals to Multiple Bonds.—W. Schlenk, J. Appenrodt, A. Michael, and A. Thal.—It has already been shown that the carbonyl group, containing the carbon

oxygen double bond, possesses the power of forming addition products with the alkali metals, and the authors have now found that in suitable experimental conditions other double bonds can be saturated by the alkali metals. The alkali metal is best used in the form of powder, and it is essential that the action should take place in absence of air and moisture. The best solvent to use is ether, and the action may be allowed to take place at room temperature. The rates at which the reactions occur differ very much; in some cases the action begins as soon as the substances are brought into contact, while in others they have to be shaken together for days. Metallic addition products of substances containing the following groups have been prepared:— $>C=C-$ (e.g., disodium stilbene, $C_6H_5 \cdot CHNa \cdot CHNa \cdot C_6H_5$); $>C=N-$ (e.g., disodium anilino-diphenyl-methane, $(C_6H_5)_2CNa \cdot NNa \cdot C_6H_5$); $-N=N-$ (e.g.,—

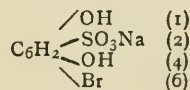


$>C=O$ (e.g., disodium benzhydrol, $(C_6H_5)_2C < \begin{smallmatrix} O \\ Na \end{smallmatrix}$).

Remarks on G. Steimmig's Article "Synthetic Rubber from Isoprene."—C. Harries.—According to Steimmig (*Ber.*, 1914, xlvii., 350; *CHEMICAL NEWS*, 1914, cix., 156) no artificial rubber has been prepared from isoprene which exactly resembles natural rubber, the product being always a mixture of 1.5- and 1.6 dimethylcyclooctadiene-1.5. The author, however, states that he can prove that the artificial rubber which he obtained in the autumn of 1909 from the Elberfelder Farbenfabriken, does not possess the composition described by Steimmig, but is a fairly pure polymeric 1.5-dimethylcyclooctadiene.

Bulletin de la Société Chimique de France.
Vol. xv-xvi., No. 3, 1914.

Monobromsulphonic Hydroquinones and their Transformation into Monobromsulphoquinones.—A. Seyewetz and J. Paris.—A sulphonic bromohydroquinone can be prepared by sulphonating the bromohydroquinone obtained by the action of bromine in solution in chloroform upon hydroquinone dissolved in a mixture of ether and chloroform. The aqueous solution of this sulphonic bromohydroquinone immediately reduces silver nitrate in the cold. It can be transformed into bromosulphonic quinone by oxidising with sodium bichromate and sulphuric acid at about 20° . Bromosulphonic quinone is a strong oxidising agent and immediately liberates iodine from an acid potassium iodide solution in the cold. When concentrated hydrobromic acid acts on sulphonic quinone below 20° —



is obtained. Above 20° 2.6-dibromohydroquinone is obtained.

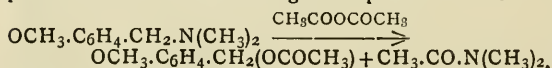
No. 4, 1914.

Absorption of Ultra-violet Rays by Coloured Organic and Mineral Solutions.—MM. Massol and Faucon.—The twenty-one dyes investigated by the authors can be classed in two categories:—(i.) Those which absorb only radiations of short wave-length and exhibit unilateral absorption. These include Paris violet, erythrosine, eosine, acid fuchsine, &c. (ii.) Those which exhibit bilateral absorption, e.g., malachite green, auramine, &c. The substances which best cut off the invisible ultra-violet rays are the yellow chrysoine, naphthol yellow, yellow potassium chromate, potassium ferrocyanide; and the reds, bordeaux B, solid red, crystallised ponceau, scarlet R.

Preparation of Cyanuric Acid from Urea and Chlorine.—A. Béhal.—The best method of preparing cyanuric acid from urea and chlorine is as follows:—600 grms. of commercial urea are heated to 110°, and dry chlorine (obtained from 320 grms. of potassium permanganate and 1600 cc. of hydrochloric acid) is led in. The temperature is then raised to about 150°, and, after the mass has become practically solid, to 180°. Finally a solid mass weighing 700 grms. is obtained. This is powdered and heated till alkaline gas is no longer evolved (loss of weight = about 100 grms.). The mass is then extracted with boiling water, and ammonia and ammoniacal copper sulphate are added. The precipitate formed is washed and decomposed with nitric acid. The raw crystallised cyanuric acid obtained is fractionally recrystallised. The first product of the reaction is chlorourea, which probably reacts with the urea to give biuret. From the biuret and urea a triuret may be formed, and this liberates ammonia and gives the cyclic product cyanuric acid.

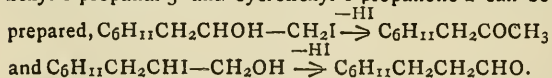
Synthesis with Isobutyrylone.—MM. Murat and Amouroux.—Isobutyrylone condenses like butyrylone with different types of organomagnesium compounds to give the tertiary alcohols and their derivatives foretold theoretically. The yields are generally lower in this new series. The alcohols obtained are heavier than those prepared from butyrylone, and the index of refraction is a little higher. The phenylurethanes of these alcohols cannot be obtained owing to the ease with which they are dehydrated, but they are well defined by their physical constants and by their decomposition products.

Action of Anhydrides and Acid Chlorides on Tertiary Benzylamines.—M. Tiffeneau and K. Fuhrer.—The anhydrides and acid chlorides are capable of breaking the bond between the atoms of nitrogen and carbon in various tertiary amines. Thus by heating *p*-methoxybenzylidimethylamine with acetic anhydride to the boiling-point of the latter the following decomposition occurs:—



The corresponding primary and secondary amines do not undergo the similar reaction, but simply give amides. Only the compounds of the structure $\text{Ar} \cdot \text{CH}_2 \cdot \text{NRR}'$ can have their nitrogen-carbon bond broken thus. Apparently chlorides and anhydrides only induce the rupture of the nitrogen-carbon bond in tertiary benzylamines because they are relatively feeble reagents, and it is only when the benzyl group is substituted that the decomposition can be brought about by simply heating to the boiling-point of the reagent. With unsubstituted benzylamines the reaction is always incomplete, and it is necessary to heat for a long time in a sealed tube.

Iodohydrines and Alkylidohydrines Derived from Cyclohexylpropene.—B. de Ressaygues.—Hypiodous acid and its ethers can be fixed at ethylene double bonds in two ways. The author has studied its action upon a mixed cyclic aliphatic hydrocarbon cyclohexylpropene, and has obtained two different compounds, from which cyclohexyl-1-propanal-3 and cyclohexyl-1-propanone-2 can be



Barium Chloride Method of Determining Free Alkali in Soda and Soap.—André Kling, Victor Genin, and D. Florentin.—The barium chloride method of determining free alkali in soda, as described in the text-books, is incapable of giving accurate results if such salts as sodium silicate or sodium borate are present. It is quite accurate, however, if the precipitation is effected in alcoholic solution. The same method can be used for the analysis of soaps containing borates or silicates; there is, however, no object in employing it if the soaps contain only fatty ether and especially oleates, the solubility of barium oleate in alcohol being appreciable.

MISCELLANEOUS.

The Chemical Laboratory Fresenius at Wiesbaden.—During the Winter Term 1913-14, the Chemical Laboratory Fresenius was attended by 29 students (including 7 ladies). Of these 21 were from Germany, 3 from Luxemburg, 2 from Russia, 1 from England, 1 from Switzerland, and 1 from Brazil. There were two assistants in the Instruction Laboratory, and twenty-nine in the private Laboratories (Versuchsstationen). To the teaching staff of the Institution belong the Directors, Geh. Regierungsrat Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, and also Dr. R. Fresenius and Dr. L. Grunhut. The next Summer Term begins on April 24. Ladies are admitted as students. During the Winter Term 1913-14, besides the scientific work, a great number of analyses were undertaken in the different departments of the Laboratory (Versuchsstationen) on behalf of trade, manufacture, mining, agriculture, hygiene, justice, and government.

Royal Institution.—The following are the lecture arrangements at the Royal Institution, after Easter:—Dr. Walter Wahl, two lectures on "Problems of Physical Chemistry—(1) Study of Matter at High Pressures; (2) Structure of Matter at Low Temperatures" (experimentally illustrated). Prof. W. Bateson, Fullerian Professor of Physiology, Royal Institution, two lectures on—(1) "Double Flowers," (2) "The Present State of Evolutionary Theory." Prof. D'Arcy W. Thompson, two lectures on Natural History in the Classics—(1) The Natural History of the Poets Homer, Virgil, and Aristophanes; (2) The Natural History of Aristotle and of Pliny." Prof. A. Fowler, two lectures on "Celestial Spectroscopy—Experimental Investigations in connection with the Spectra of the Sun, Stars, and Comets." Three Literary Lectures. Prof. Svante Arrhenius, three lectures on "Identity of Laws in General and Biological Chemistry." Prof. Silvanus P. Thompson, two lectures on "Faraday and the Foundations of Electrical Engineering." Dr. T. E. Stanton, two lectures on "Similarity of Motion in Fluids—(1) The Theory of Similarity of Motion in Fluids and the Experimental Proof of its Existence; (2) The General Law of Surface Friction in Fluid Motion." Prof. C. J. Patten, two lectures on "Bird Migration." Prof. J. W. Gregory, two lectures on—(1) "Fiords and their Origin," (2) "Fiords and Earth Movements." Mr. Sigismund Goetze, two lectures on "Studies on Expression in Art—(1) Origin and Development, (2) Right Expression in Modern Conditions." The Friday Evening Meetings will be resumed on April 24, when the Astronomer Royal, Mr. F. W. Dyson, will deliver a Discourse on "The Stars around the North Pole." Succeding Discourses will probably be given by Mr. E. H. Benson, Prof. Karl Pearson, Prof. F. Keeble, Mr. Robert Mond, Prof. J. C. Bose, Prof. W. H. Bragg, and other gentlemen.

NOTES AND QUERIES.

* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Mercury Fulminate.—I should be obliged for information as to bodies formed when fulminate of mercury is dissolved in a solution of sodium thiosulphate. The equation is also requested, as I have looked in numerous text-books in vain.—F. O.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Royal Institution, 5. General Meeting.

Society of Chemical Industry, 8. "By-Products from Peat," by F. Mollwo Perkin. "Sulphuric Acid—the Swing of the Pendulum," by H. E. Armstrong. "Table of Specific Gravities of Spirits for Use with Bedford's Tables," by J. N. Rakshit and S. N. Sinha. "Viscosity of Rubber Solution," by R. Gaunt.

THE CHEMICAL NEWS.

VOL. CIX., No. 2837.

ATOMIC WEIGHTS.

By F. H. LORING,

THE study of radio-active phenomena affords strong evidence that many of the stable elements are complex, in that they comprise atoms differing in atomic weight from each other which are non-separable by chemical means. Prof. Soddy gave expression to this idea (CHEM. NEWS, cviii. 168).

The discovery of a companion gas to neon of different atomic weight, yet spectroscopically indistinguishable, and the supposition that certain radio-elements, although differing materially in atomic weight, are indistinguishable by this test (supported by one definite experiment), is in harmony with the belief that the atom is conditioned by the electron rather than by its atomic mass. The mass may, as it were, be the vehicle for retaining the electron or electrons. As a radio-element loses β -particles (negative electrons), its chemical properties become altered without an appreciable alteration in its mass. It is true that the loss of an α -particle (=helium atom carrying two positive charges of electricity) coincides with a change in properties, but probably there is a rearrangement of the electrons in the atom in this case. As the loss of two positive charges alters the chemical character of the atom, it might be inferred that the loss of two negative charges would restore the atom to its original chemical state. A stepping-back of the element in the Periodic Table, in consequence of the loss of a β -particle, has been observed (see citation above).

If, therefore, the electric system within the atom is a real differentiating factor, then it seems probable that the fractional atomic weight values in themselves are of no material moment, and one might conceive the elementary atomic weights as whole numbers. Moreover, these numbers, to be in harmony with the radio-elements, should differ by four units, being built up of helium atoms. The possibility of H_3 as a nucleus in the odd-number series (see below) suggests itself.

This idea would reconcile the Prout theory that all the elements are fixed or stable polymerides of hydrogen as a fundamental unit, hydrogen being taken, however, as absolute unity. Then helium itself may be four atoms of hydrogen combined in such a way as to be extremely stable. The existence of X_3 discovered by Sir J. J. Thomson, which is now believed to be a polymeride of hydrogen, supports this conjecture, since this tri atomic molecule is fairly stable. H_4 , therefore, might be even more stable, and thus become the helium atom.

I have shown in the CHEMICAL NEWS, cix., 143, that copper, silver, and gold probably are made up of associate elements (atoms) differing in atomic weight, non-separable by chemical means, and exactly whole numbers. This idea in a general way was suggested by Sir William Crookes (see CHEM. NEWS, 1887, lv., 95).

In this connection it may be of interest to note that P. de Heen (*Bull. Acad. Roy. Belg.*, 1913, pp. 680-694) gave an experimental demonstration of the variability of the molecule and atom. The facts brought to light seem to show that the silver-chloride molecule can be modified by suitable treatment, and that the different forms of silver salt are to be regarded as derived from silver atoms which are not identical. In other words, the experiments seem to afford evidence of transformation of normal silver into its meta elements. Whether this experiment is to be interpreted in this particular way need not be discussed here, suffice it to say that the idea of meta elements is one that is no doubt engaging the attention of many scientists.

The meta elements of Crookes correspond with the isotopes of Soddy.

It will be seen that probably the chemical elements can be broadly classified thus:—

I. Whole-number atomic-weight elements which have no associates differing from them in atomic weight.

II. Whole-number atomic-weight elements composed of, or containing, chemically non-separable associates of different atomic weight.

If the foregoing argument be sound in principle, then the atomic-weight values, as determined experimentally by chemical methods, should be verifiable, and the values for the associate members ascertainable. The associates or isotopes may be designated thus:— Cu^I , Cu^{II} , Ag^I , Ag^{II} , &c. The true atomic weights may be correspondingly expressed thus:— Cu^{I63} , Cu^{II67} , &c. Furthermore, the relative numbers of respective atoms may be shown thus:— Cu^{I63} , Cu^{II67} , Ag^I107 , Ag^{II112} , &c.

Group VII. is very interesting, as it contains, in my opinion, branches (see "Studies in Valency," pp. 23 and 25), and I have attempted to ascertain the various values for this curious group. A word of caution is, however, necessary. The method employed renders it difficult to fix upon the proportionate numbers, and doubt arises as to whether one is justified in confining the selection of whole numbers to the Rydberg Atomic Series. When this series fails to supply a proper figure, other whole numbers may be taken. This procedure may be objected to, but it is not safe to be influenced too strongly by the radio-active precedent. Square brackets will be introduced to designate those values which are not taken from the Rydberg series.

The following tentative values have been worked out by this method:—

Chlorine	=	$(40 \times I + 35 \times IO)/II$	=	35'4545
Manganese	=	$(54 \times I + 55 \times IO)/II$	=	54'90
Iron	=	$(55 \times I + 56 \times IO)/II$	=	55'90
Nickel	=	$(55 \times I + 59 \times IO)/II$	=	58'63
Cobalt	=	59'00		
Ruthenium	=	$(99 \times I + [102] \times IO)/II$	=	101'72
Rhodium	=	$(100 \times I + 103 \times IO)/II$	=	102'72
Palladium	=	$(104 \times I + 107 \times IO)/II$	=	106'72

Commenting on the above atomic-weight values it will be observed that they agree with the experimental ones, and in some cases the same atomic weight is common to two or three elements. This peculiarity would be considered as fatal to the scheme, if it were not for parallel cases amongst the radio-elements, suggesting that though the atomic weights are the same, the electronic or electric systems differ in the atoms, and indeed they would not therefore be isotopic.

Referring to the radio-group, it will be seen that perhaps Hönigschmid's value for radium, 225'97, is near to a possible true value 226, but a question arises as to whether the disintegration is quite as simple as supposed, considering that associate atoms may in some way alternately disintegrate, as suggested by the branching in the different series.

The radio-active gases, and the inactive gases which are not radio-active, should give, by the positive ray method, double lines if these elements be mixtures unless some unsuspected condition arises. The lines might be so close as to appear as one line if the atomic weights of large magnitude differ by only one unit. Ten argon atoms of atomic weight, 40 each to every 1 of atomic weight 39, would give a mean value of 39'909. Similarly, krypton would be 82'909. But in the latter case a non-Rydberg value, 82, would be introduced. It seems probable that the positive-ray experiments will throw some light upon the question of meta elements.

I may add in conclusion that, using the constants 10 and 1, the following mean values are obtainable:— $Mg = 24'27$; $Si = 28'27$; $Br = 79'909$; $Ba = 137'36$. With the constants 1 and 7, $Al = 27'125$. Constants 3 and 7 are possible ones for some of the rare earth metals.

It seems significant to observe that aluminium and magnesium are the first elements in the odd and even series which have well-authenticated fractional differences of appreciable magnitude, implying in the case of aluminium that possibly it is made up of six helium atoms condensed round a H_3 -nucleus ($=27$), and in association with a helium polymeride without such a nucleus ($=28$) in proportion 7:1. The preceding elements therefore may be fundamental types (I.), whilst the succeeding ones are for the most part more complex (II.). Assuming a continuation of the atomic disintegration process, it should then stop at these elements.

March 22, 1914.

SOME NOTES ON THE ESTIMATION OF PHOSPHORUS IN IRON AND STEEL.

By HARCOURT PHILLIPS, F.C.S.

OF the various schemes from time to time proposed for estimating phosphorus in steel, the chief are those based on initial separation of the element as phospho-molybdate salt, from a solution containing free nitric acid and ammonium nitrate. The details of the process are set forth in the text-books dealing with the requirements of a steel works laboratory.

The general experience of analysts has confirmed the observation that to ensure entire separation of the phosphorus in a minimum of time, the volume of solution should be neither too large nor the nitric acid in too great excess. Violent agitation and the presence of a fair amount of ammonium nitrate much assist speedy precipitation. Fresenius gives $40^\circ C.$ as a suitable temperature, and, after vigorous stirring of the solution, sets it aside for twelve hours; a plan of working probably designed to lessen the chance of co-precipitating molybdic trioxide and at the same time ensure complete separation of all phosphorus.

My own experience I expect will be that of other analysts, viz., that a sufficiency of molybdate reagent assisted by vigorous agitation will separate all phosphorus after twenty minutes.

Precipitation of phosphoric acid from iron and other metals by molybdenum was a plan worked out by Sonnenschein (*Journ. Prakt. Chem.*, liii., 342), and has been practised for over fifty years, though the constitution of the yellow precipitate was, until recently, imperfectly known. In recent years F. Hundeshagen (*Zeit. Anal. Chem.*, xxviii., 141) has carefully examined the precipitate to learn its composition, and the conditions in which the pure phospho-molybdate is formed. Hundeshagen (*loc. cit.*) describes the precipitate, and assigns the formula $(NH_4)_3PO_4 \cdot 12MoO_3$, a salt with a phosphorus content of 1.65 per cent when dried at $130^\circ C.$ or thereabouts.

Brearley and Ibbotson ("Analysis of Steel Works Materials," p. 344) give an abstract of Hundeshagen's paper.

The yellow precipitate, once obtained and washed free from acid and other matter, can be dealt with in one of several ways. A common practice is to collect it on a previously weighed or counterpoised filter-paper, to wash with dilute nitric acid, then alcohol, and to dry in water-oven, and re-weigh. The phosphorus content is found by the factor 0.0165. This process is usually called the "direct method," to distinguish it from those wherein the washed precipitate is either dissolved in ammonia, and treated as by Brearley and Ibbotson's lead molybdate plan, or, again, is dissolved in soda as in J. O. Handy's scheme (*CHEMICAL NEWS*, lxxvi., 324). A further indirect plan is that described in Blair's "Chemical Analysis of Iron" (1908, p. 93), in which the phospho-molybdate is reduced by Zn and H_2SO_4 , and the solution titrated with permanganate. Other indirect methods are based on the initial separation of the phosphorus by means of stannic oxide,

ferric oxide, &c., with conversion of the resultant phosphate into ammonium magnesium phosphate, and final weighing as $Mg_2P_2O_7$.

Schemes such as these are far too slow for a busy works analyst. In the course of my practice I have employed the "direct method" for some years, and presume that other analysts will have observed, as I have, the appearance of a greyish blue stain on the dried filter-paper. The stain appears above the precipitate, sometimes on the outside, and often at the apex of the filter. The stain suggests slight reduction of the MoO_3 by the cellulose. Should the stain be well developed the paper will be friable and break easily at the apex.

I may say that the stain seldom appears unless there be a remnant of nitric acid in precipitate or paper, or unless the filter and precipitate have lain too long in the water-oven. Should the stay in the oven have been unduly prolonged some stain will always appear, though the paper and precipitate shall have been copiously washed with cold water to ensure complete removal of acid.

The gradual loss of weight which a filter and precipitate sustain by prolonged drying is shown by the following examples:—

The phospho-molybdate from 2 grms. of separate steels was collected and thoroughly washed on previously dried and weighed 7 cm. filters. The final wash was with alcohol.

	A.	B.
Weight of precipitate after quarter of an hour in oven	0.0361	0.031
Weight of precipitate after one hour in oven, stain slight	0.0349	—
Weight of precipitate after three hours in oven, stain more developed	0.0324	0.028

Taking 0.0361 gm. in Sample A to be correct, the phosphorus will be 0.0297 per cent.

This steel, by Ibbotson's lead molybdate method, gave 0.030 per cent, and by the magnesia plan on 4 grms. of the metal 0.0307 per cent phosphorus.

It would appear, then, that after the final wash with alcohol the filter should not stay in the water-oven longer than fifteen to twenty minutes.

It was the appearance of the stain which led me to try an alternative plan of dealing with the precipitate, a plan I will now describe.

The following solutions were prepared:—

Di-sodic phosphate.

Nitro-molybdate.

Nitric acid, 1.2 sp. gr.

A 2 per cent nitric acid wash.

A sodium silicate solution, of which 5 cc. contained $SiO_2 = 3$ mgrms. Si.

A mean of four estimations of the phosphorus in 50 cc. of the sodic phosphate by the magnesia plan gave 0.00798 gm. The solution was measured in all cases from a burette divided into one-tenth cc. and fitted with a float.

The nitro-molybdate was prepared according to the formula given by Brearley and Ibbotson on p. 56 of their book. When made as they direct the solution will remain quite free of deposit for many weeks. The sodium silicate was acidified with nitric acid immediately before use, and was a quite clear solution.

The procedure was this:—After measuring off 50 cc. of the phosphate into a stoppered flask there were added 30 cc. of the 1.2 HNO_3 , 10 cc. of ammonia (0.880 diluted with an equal volume of water), and then 30 cc. of the molybdate. After vigorous shaking and warming to $40^\circ C.$ the flask was set aside for an hour before filtration of the liquid, though the upper layer had cleared in fifteen minutes. The precipitate, collected on a 9 cm. filter of close texture, was freed of all salts by aid of the 2 per cent nitric acid wash. This done, *all acid* was then removed by washing with cold water. (The filtrate will usually be quite clear, provided the paper has the requisite texture and has been snugly adjusted, when wet, to the side of the

funnel). On completion of the washing the funnel was placed over a 6½ cm. light weighed dish, and the precipitate dissolved from the filter by ammonia.

What precipitate remained in the flask was collected in the same manner and added to the contents of the dish, which need not exceed 30 cc. if the washing has been done with small affusions at a time of hot water. The contents of the dish, after being taken to dryness on the steam-bath, were further heated in the water-oven until the residue had a constant weight.

Whatever the exact composition of the saline residue may be, it will contain the phosphorus of the 50 cc. of standard phosphate, viz., 0.00798 gm., so that, given concordant weights of residue, the operator can deduce a factor therefrom.

A first experiment gave me 0.534 grm. of residue, hence $\frac{0.00798}{0.534}$ gives the factor 0.01494. An average of six experiments gave 0.0151, of which the highest was 0.0152 and the lowest 0.0148.

For the experiments to follow, chiefly made with measured portions of the standard phosphate, I calculated the phosphorus content by the factor 0.0151. I should state that the ammoniacal solution of the phospho-molybdate was in all cases re-filtered through the same filter before evaporating, when iron was present. The precaution is necessary, since some little iron is co-precipitated with the phospho-molybdate, and clings to it or to the paper in spite of the washing with the 2 per cent nitric acid.

Na ₂ HPO ₄ solution. Cc.	Phosphorus taken. Grm.	Weight of residue dried at 100° C.	Phosphorus per cent assumed taking 2 grms. of a steel.	Phosphorus per cent found by experiment.
20	0.003192	0.2120	0.1596	0.1600
10	0.001596	0.1074	0.0798	0.0810
10	0.001596	0.1080	0.0798	0.0815
5	0.000798	0.0532	0.0399	0.0401
5	0.000798	0.0525	0.0399	0.0396
2.5	0.000399	0.0270	0.0199	0.0203
2.5	0.000399	0.0275	0.0199	0.0207
2.5	0.000399	0.0281	0.0199	0.0212
2.5	0.000399	0.0268	0.0199	0.0202
2.5	0.000399	0.0269	0.0199	0.0203

The annexed estimations of phosphorus were made in the presence of as much ferric nitrate as would be equal to 2 grms. of iron. In the first four experiments soluble silicic acid equal to 3 mgrms. of Si were added. This would represent 0.15 per cent of Si in a steel, and the precipitated phospho-molybdate was collected after one hour's standing. In the second four experiments *a*, *b*, *c*, and *d*, soluble SiO₂ equal to 12 mgrms. of Si was added, and the precipitate allowed to stand for twelve hours before filtering. After weighing the saline residues I dissolved them in ammonia, and set the solution aside until next day. A slight flocculent deposit was then observable, in which I confirmed the presence of silica and iron. I am not inclined, however, to attribute the higher percentage of phosphorus in *a*, *b*, *c*, and *d* entirely to the above, since the error may be partly ascribed to co-precipitated molybdic trioxide—an effect of the twelve hours repose.

Na ₂ HPO ₄ solution. Cc.	Phosphorus taken. Grm.	Weight of residue dried at 100° C.	Phosphorus per cent assumed taking 2 grms. of a steel.	Phosphorus per cent found by experiment.
10	0.001596	0.1090	0.0798	0.0822
5	0.000798	0.0533	0.0399	0.0402
5	0.000798	0.0540	0.0399	0.0407
5	0.000798	0.0566	0.0399	0.0427
5	0.000798	0.0634	0.0399	<i>a.</i> 0.0478
5	0.000798	0.0584	0.0399	<i>b.</i> 0.0440
5	0.000798	0.0624	0.0399	<i>c.</i> 0.0471
5	0.000798	0.0605	0.0399	<i>d.</i> 0.0456

In conclusion, I will give the estimation of phosphorus in a chromium steel. The test was made by four methods. For the magnesia method 5 grms. of steel were taken.

Phosphorus, per cent.

Direct plan		0.0178
Ibbotson's plan		0.0180
J. O. Handy's plan		0.0177
Magnesia plan		0.0182
H. Phillips's plan		0.0181

As regards speed, the quickest is perhaps Handy's plan. When making use of it I find it convenient to balance the acid and alkali cc. to cc., and to check occasionally the strength of the soda by means of freshly precipitated and washed phospho-molybdate, which is readily prepared by aid of a standard di-sodic phosphate, of which 50 cc. represent 8 mgrms. of phosphorus.

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AN EXPERIMENT ON THE COLOURS OF SOME COBALT SALTS IN SOLUTION.

By J. E. MARSH.

A SOLUTION of sodium chloride and cobalt chloride in a mixture of water and acetone, which is pink when cold, separates on warming into two solutions, the upper one being light blue in colour and the lower dark blue. The upper layer is expelled gradually, and the lower layer changes its colour gradually as the temperature is raised. The solutions will mix again on cooling to the original homogeneous pink solution. When cooled without mixing the upper layer fades to an almost colourless solution, which becomes blue again on warming, while the lower layer changes in colour from blue to pink. The concentration of the solution may be varied within certain limits. A good effect is given by taking the following proportions by weight:—1 Sodium chloride; 2 hydrated cobalt chloride, CoCl₂.6H₂O; 7.7 acetone; and 8.7 water. This solution contains the salts in the proportion of 2NaCl to CoCl₂, and about equal volumes of acetone and water. The solution separates on heating into nearly equal volumes, and the colours are not too dark. The solution should be contained in a sealed glass tube and heated by placing in hot water. Cobalt chloride alone without the sodium chloride will bring about the separation in much the same way, but a higher temperature is required.

Potassium and cobalt bromides in acetone and water give much the same effect. With lithium and cobalt chlorides the solution when cold is blue. On warming, the light and dark blue layers are obtained, and on cooling without mixing the upper layer retains its colour, while the lower layer changes from blue to pink. The following proportions by weight give a good colour effect:—1 Lithium chloride; 2.8 hydrated cobalt chloride; 9.7 acetone; 10.5 water.

AN ENCLOSED CADMIUM ARC FOR USE WITH THE POLARIMETER.*

By T. MARTIN LOWRY and H. H. ABRAM.

It is no longer necessary at the present time to emphasise the importance of rotatory dispersion, *i.e.*, of measuring rotatory powers for a whole range of wave-lengths, instead of recording only one point on an unknown curve. But as regards methods of measurement, the necessity of using pure monochromatic light may still be urged. Light filters must be regarded as suited only for a first approximation, since the optical mass centre of the transmitted light may vary with the source of light, and in any case it is impossible to get exact readings of big

* Contribution to a General Discussion on "Optical Rotatory Power," held before the Faraday Society, March 27, 1914.

rotations, which no longer give an extinction. Spectral purification of white light is better, but the "monochromatic illuminator" requires careful use to be sure that the wave-length used is actually that recorded on the drum of the instrument.

In the early days of the measurement of rotatory dispersion it was necessary to use a large range of wave-lengths, as the form of the curves was quite unknown. Thus, in 1908, measurements of the rotatory power of methyl camphorcarboxylate were given for 26 wave-lengths, namely:—

Li, 6708. Na, 5893. Tl, 5351.
Hg, 5790, 5769, 5461, 4359.
Cd, 6438, 5086, 4800, 4678.
Ag, 5469, 5209. Zn, 6364, 4811, 4722, 4680.
Cu, 5782, 5700, 5219, 5154, 5105, 4705, 4651, 4587, 4378.

Twenty-four wave-lengths were used in measuring the rotatory power of quartz in the visible region of the spectrum, and readings (as yet unpublished) have been taken by a photographic method for over 700 wave-lengths in the visible and ultra-violet regions of the spectrum.

In the case of substances whose rotatory dispersion is anomalous, it is still desirable to extend the observations to include a large number of wave-lengths, extending over a wide range of the spectrum. But in the case of substances whose rotatory dispersion is normal a much smaller range of wave-lengths will suffice; in fact, in the case of all those substances whose rotatory power can be expressed by the simple formula—

$$\alpha = \frac{k}{\lambda^2 \lambda_0^2}$$

only two observations are required in order to determine the two constants of the equation. These two fundamental observations are most conveniently made with the green and violet rays of the mercury spectrum, since the ratio $\alpha_{4850} / \alpha_{401}$ is something like 10 times more sensitive than, e.g., the ratio $\alpha_{5461} / \alpha_{5893}$. The simple apparatus required for measuring this ratio is being exhibited by the courtesy of Messrs. A. Hilger, who have supplied the polarimetric equipment, and the Westinghouse Cowper-Hewitt Co., who have supplied the mercury-lamp.

It still remains, however, to establish a satisfactory method of proving that the curve of rotatory dispersion is strictly normal. This can be done to a rough approximation by reading one or two additional wave-lengths and then plotting $1/\alpha$ against λ^2 , when the whole of the readings should fall upon a straight line. The most convenient readings to take for this purpose are Na 5893 and Li 6708. But the sodium line is too near the mercury-green to reveal any but the grossest anomalies, and the lithium line, which represents the "furthest south" in the direction of the infra-red, cannot be relied on to give readings of the same order of accuracy as in the case of the two mercury lines. The simple formula given above was therefore verified in the first place only when the readings for 23 substances of similar dispersive power were averaged in order to eliminate individual errors of observation. It was at this point that the enclosed cadmium arc made its appearance, with the result that it promises to effect a revolution in polarimetric methods comparable with that which resulted from the introduction of the mercury arc.

The methods by which the cadmium spectrum was first rendered available for polarimetric work in the visible region were shown before the Physical Society in June, 1909, and were described in a paper which was published in the *Proc. Phys. Soc.*, vol. xxii., and also in the *Phil. Mag.* of August, 1909. The apparatus consisted of two electrodes of a silver-cadmium alloy, rotating in opposite directions on spindles driven from a small electro-motor. On striking an arc between the electrodes a brilliant spectrum was emitted which included the lines of

silver and of cadmium. Apart from the annoyance caused by the flickering of the arc this apparatus can be used very effectively if the polarimeter is provided with a constant-deviation spectroscope to purify the light before it enters the polariser. But it cannot well be used with the simpler apparatus, in which the light is resolved only by a direct-vision prism on the eye-piece, as the unextinguished parts of the spectrum are usually too dazzling to permit of easy reading on any one line at the extinction-position. The "method of producing an intense cadmium spectrum" by means of a silver-cadmium arc was therefore "not put forward as the ideal way of producing an intense cadmium spectrum, but rather as an intermediate stage in the development of the perfect cadmium lamp of the future." The search for the perfect cadmium lamp has been in progress ever since, and by the generous co-operation of Mr. F. Stanley, of Messrs. A. Hilger & Co., we are able to exhibit—not perhaps the perfect lamp itself, but one of its more or less distant ancestors in the process of its evolution.

In the lamp the arc is run between water-cooled electrodes of solid cadmium; this is important, partly because it checks the vaporisation of the metal, but mainly because if the metal is allowed to melt it is liable to crack the tube whenever the lamp is started or stopped. The lamp must be used in conjunction with a Gaede pump, as the metal gives off considerable quantities of gas under the influence of the electric discharge, and these must be pumped off in order to maintain the vacuum. Occasionally, when the vacuum is good, the arc will start itself by merely switching on the current, but usually it is necessary to start the arc by a spark; this can be done conveniently by connecting the electrodes to the inner walls of two Leyden jars and connecting the outer walls to the secondary terminals of an induction coil. The light emerges through two windows of quartz. In our most recent lamp we have tried to protect these windows from condensed metal by water-jacketing the ends of the tube to which they are attached, but the water-jacketing must not extend to the central part of the tube, which must remain hot in order to prevent the formation of a conducting bridge of condensed metal. An arch of silica has been provided to bring the arc to the centre of the tube.

The lamp will burn quite well under a pressure of 100 volts, but it has a longer life if the voltage is higher, owing to the fact that an arc of greater length can be kept alight. The extinction of the lamp on the lower voltages is caused most frequently by the distillation of mercury from the electrodes, which thus become shortened unduly. We have tried to check this defect by enlarging the diameter of the tubes containing the metal, but have not yet had enough experience to say how far we have been successful in our endeavours.

The cadmium lamp, which is still in the experimental stage and obviously far from perfect, is only just being brought into actual use in our polarimetric work. We can, however, quote one example of the kind of service it may be expected to render. It was desired to find out in the case of α - and β -methyl-glucosides, not merely the magnitude of the constants in the dispersion-equation, but also whether these two compounds, containing no less than 5 asymmetric carbon atoms, nevertheless obey rigidly the simple dispersion law. Solutions of the two glucosides were made, containing 25 grms. in 100 cc., and these were examined in 600 mm. polarimeter tubes. The readings were as follows:—

	α -Methylglucoside.	β -Methylglucoside.
Mercury	Violet.. 155.32° Ratio	33.32° Ratio
	Green.. 94.17 1.649	19.95 1.666
Cadmium	Green.. 109.90 Ratio	23.51 Ratio
	Red .. 66.10 1.663	14.09 1.669

It will be seen that the ratios for the two cadmium lines are almost equal to the ratios for the two mercury

lines. Each pair of lines can be read without disturbing the setting of the apparatus, and the cadmium readings (unlike those for lithium) are quite as reliable as the mercury readings and equally suited for working out the "rotation constant" k , and the "dispersion constant" λ_0^2 , for either substance. The values of the constants are:—

	k .	λ_0^2 .
<i>a</i> -Methylglucoside—		
From mercury readings ..	25.87°	0.0234
From cadmium readings ..	25.85°	0.0235
<i>β</i> -Methylglucoside—		
From mercury readings ..	5.40°	0.0274
From cadmium readings ..	5.48°	0.0257

The figures for the *a*-methylglucoside are remarkable. The "rotation constant" k (which is numerically equal to the "absolute rotation," α_0 , *i.e.*, the rotation which would be observed at wave-length $\lambda = \sqrt{1 + \lambda_0^2}$) is represented by two values which differ from the mean by only $\pm 0.01^\circ$, an error of 1 part in 2000. The "dispersion constant," which shows a difference of one unit in the third significant figure, is really (in spite of appearances) still more accurate. Three units in this decimal correspond with a difference of one unit in the fourth figure of the dispersion ratios; the two values given for λ_0^2 correspond therefore with a difference from the mean of 1 part in 10,000 in the actual readings. There can therefore be no doubt whatever as to the validity of the simple dispersion formula to represent the experimental data for this complex substance.

The figures for the *β*-methylglucoside are less concordant, in part because the readings are five times smaller; but they agree sufficiently well to show that there is no large deviation from the simple dispersion law.

It will be seen from the illustrations given above that the development of the enclosed cadmium arc promises to inaugurate a new era in the measurement of *normal rotary dispersion*. With the help of the new apparatus it will be possible to determine the two fundamental constants of any optically active compound by two methods of equal exactness. Further, the agreement of the two pairs of figures will serve as a check, not merely on the accuracy of the readings (in itself a very important advantage), but also on the strict validity of the dispersion formula in the case of each individual substance.

It is a pleasure, in conclusion, to acknowledge the valuable help that has been received in connection with this work from the Dixon Fund of the University of London.

DETERMINATION OF WATER OF CRYSTALLISATION IN SULPHATES.

By S. B. KUZIRIAN.

CERTAIN substances, *e.g.*, chlorides of barium and calcium, sulphates of sodium, potassium, barium, &c., are completely dehydrated at moderately high temperatures, leaving a definite and weighable compound. Under such conditions, when the substances do not lose anything but water, at a definite temperature, the determination of water of crystallisation can be made with great ease.

Certain other substances, like the minerals talc, topaz, chondrodite, staurolite, do not lose all of the water of crystallisation by simple ignition at moderate temperatures. The high heat of the blast-lamp is in such cases applied for the complete removal of water. This latter step often gives rise to complications when the material to be blasted changes weight otherwise than by loss of water, *e.g.*, by loss of carbon dioxide, fluorine, chlorine, or by accession of oxygen, as when a ferrous compound is ignited in air.

Some other crystalline substances like sulphates and alums of aluminium and chromium are decomposed with loss of material other than water, at temperatures obtainable with an ordinary good-sized Bunsen burner, thus preventing a correct determination of their crystalline water.

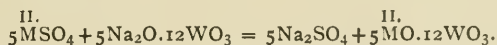
Various modifications in treatment have been suggested to avoid complication in water determinations. For instance, in the case of minerals, talc, topaz, &c., fusion with pure and dry sodium carbonate will expel the water which may be absorbed in sulphuric acid and weighed (Hillebrand, *Bull.* 422, United States Geol. Survey, p. 79).

Fusion of such silicates, very finely pulverised, with anhydrous powdered borax, is another method suggested by Jannasch ("Praktischer Leitfaden der Gewichtsanalyse," Leipzig, 1897, 2nd ed.), for the same object. If the silicates are found to contain fluorine, then a retaining layer of granular lead chromate or a previously fused and powdered lead oxide is used in the ignition tube. This process is found objectionable by W. H. Hillebrand for the reason that silicates on fine grinding lose some water (*Bull.* 422 United States Geol. Survey, p. 83).

Magnesia is another substance mentioned in connection with determination of crystalline water in decomposable compounds like silico-fluorides (F. Stolba, *Zeit. Anal. Chem.*, vii., 23). Under definite conditions this flux seems to give satisfactory results, a correction being necessary when the separated metallic oxide, *e.g.*, ferrous oxide, takes up atmospheric oxygen. In the case of decomposable sulphates, however, no attempt has been made to determine their water of crystallisation, while retaining all of the acidic oxide.

In the investigation of the action of sodium paratungstate upon some salts containing a volatile acid radical, both in presence and absence of superheated steam, described in previous papers (*Am. Journ. Sci.*, [4], xxxi., 497; xxxvi., 301, 305), it has been shown that this acidic salt is able to expel the acidic oxides of carbonates, nitrates, chlorides, chlorates, &c., completely and with great ease. But sulphates which are stable on simple ignition, for example, the sulphates of sodium, potassium, barium, and even calcium and manganese, do not lose appreciably their sulphur trioxide either in absence or in presence of superheated steam on fusion with the paratungstate. For example, 0.2 gm. of sodium sulphate on fusion with the paratungstate did not lose in weight at all. The same amount of manganous sulphate when fused with the same flux lost only 0.0010 gm. of sulphur trioxide. Calcium sulphate on similar treatment lost only 0.0002 gm., and further heating did not occasion further loss. The explanation is that the basic sodium oxide of the sodium paratungstate combines with volatile sulphur trioxide of the sulphates to form the non-volatile sodium sulphate. The presence of a considerable excess of the acidic tungsten trioxide apparently does not influence the reaction.

The following may serve as a typical representation of the reaction:—



Since sodium paratungstate does not expel the volatile sulphur trioxide from sulphates, it should be capable of serving a useful purpose as a flux in the expulsion of the water of crystallisation of sulphates ordinarily decomposable by heat; and any sodium tungstate containing less of this acidic oxide should be similarly serviceable. In the preliminary investigation of this application of the sodium tungstates a nearly neutral sodium tungstate was prepared, and a portion of the dry material was weighed and placed in a platinum crucible, a weighed portion of a decomposable sulphate—*viz.*, crystalline copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)—was mixed well with the tungstate, and the covered crucible heated with a very low flame of a Bunsen burner waving under it. (In order to purify the commercial material, which ordinarily contains sodium carbonate, it was fused in a large platinum dish over the blast, and pure tungstic trioxide was added until carbon

dioxide ceased to bubble out). After driving off most of the water, the crucible was heated to low redness and the mixture fused, cooled, and weighed. The loss apparently corresponded exactly to the theoretical loss of water in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The fusion was repeated several times and weighed over again, but no further loss in weight was found. So it appears that while crystalline copper sulphate loses some of its sulphur trioxide when heated by itself at the temperature which is necessary for its complete dehydration, no loss of the acidic oxide occurs in presence of sufficient amount of neutral sodium tungstate when the mixture is heated over a Bunsen flame to dull red heat. It is possible to keep the mixture in quiet fusion for fifteen to twenty minutes without losing any sulphur trioxide. Sodium tungstate thus serves excellently to retain the sulphur trioxide at a temperature sufficiently high to dehydrate the sulphate completely.

To determine the water of crystallisation in sulphates by weighing the water evolved, as well as by loss on ignition, the following procedure was tried. A hard glass ignition tube, about 15 inches long and $1\frac{1}{4}$ inch in diameter, was placed upon a small furnace; each end was fitted with a perforated (one hole) rubber stopper soaked in hot paraffin for a moment and wiped carefully; and one end of it was connected with a large air-drying apparatus, while the other end was joined to a sulphuric acid weighing tube. The sulphuric acid tube was connected to a calcium chloride drying tube to prevent the entrance of any moisture into the weighing tube from outside, and the calcium chloride tube was connected to an aspirator. The ignition tube was thoroughly dried by heating it for at least forty-five minutes, and passing a rapid current of dry air with the aid of the aspirator. The efficiency of the apparatus was evident from the fact that when, after such drying, the sulphuric acid weighing tube was connected with the ignition tube and a blank test made, by running the apparatus for one hour, a gain of only 0.0003 grm. in the weight of the weighing tube resulted, for which a correction was applied in the subsequent work. After having the apparatus thus in readiness, exactly half a grm. of the sulphate was mixed well with 3 grms. of sodium tungstate in a porcelain boat, ignited and weighed previously. The boat and its contents, weighed together, were introduced into the ignition tube. The ignition was started at first very gently by passing a current of hot dry air over the boat, at a rate of 3 bubbles a second, for a period of fifteen minutes. The temperature was carefully and gradually increased until the mixture went into clear fusion. By waving a Bunsen flame around the ignition tube and short delivery tubes the condensed moisture was volatilised. After the apparent disappearance of all moisture the remaining traces of it were forced into the sulphuric acid weighing tubes by a more rapid current of dry air, while continuing the heating of the ignition and delivery tubes for at least twenty minutes. After this period the heating was stopped, while a rapid current of dry air was passed for about ten minutes. The weighing tube was disconnected, stoppered with the glass plugs used as stoppers in the first weighing, brought as nearly as possible to the original temperature (by setting it aside for a few moments), wiped around with a filter-paper, and weighed. The gain in weight of the weighing tube was recorded. After disconnecting the weighing tube from the ignition tube, the delivery tube leading into the ignition tube was plugged carefully to avoid any moisture. The boat was taken out while rather hot, cooled in a desiccator over sulphuric acid, and weighed, and the loss in weight was recorded. It was found that if the procedure was carried out with the utmost care, observing all the precautions, the loss in weight of the porcelain boat, within experimental error, corresponded to the gain in weight of the sulphuric acid tube, and this corresponded closely to the theory for water in the crystallised sulphates. Repeated fusions of the contents of the boat did not occasion any further loss in weight, thus proving that under the conditions there is no loss of sulphur trioxide.

The sulphuric acid weighing tube used was a side-neck

U-tube filled with glass beads, and the ends of the large tube were sealed. The rubber connectors were air-tight so that the weighing tubes would not gain in weight over night. It is desirable that the sulphuric acid in the drying apparatus and in the weighing tube should have the same absorbing power; for this reason the sulphuric acid in the weighing tube was changed after every four determinations.

The determination of the water of crystallisation in copper sulphate and in other sulphates was carried out under the conditions cited above, with special precaution to avoid loss by decrepitation of the salt while yielding its water. After mixing the sulphate well with sodium tungstate, another portion of the flux was put upon the surface of the mixture to form a trap, and thus avoid mechanical loss, and the mixture was heated with utmost care for a long time at a temperature not exceeding 70°C . Following are some of the results obtained with various sulphates:—

TABLE I.—Determination of Water of Crystallisation in Various Sulphates.

Sulphate taken.	Dried sodium tungstate taken.	Loss of the porcelain boat after ignition.	Gain of sulphuric acid weighing tube.	Difference.
Grm.	Grm.	Grm.	Grm.	
Copper Sulphate.				
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.				
0.2000	4	0.0707	0.0701	-0.0006
0.2000	4	0.0715	0.0712	-0.0003
Aluminium Sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$.				
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$.				
0.2000	4	0.0897	0.0913	+0.0016
0.2000	4	0.0900	0.0894	-0.0006
0.2000	4	0.0907	0.0915	+0.0008
0.2000	4	0.0925	0.0935	+0.0010
Nickel Sulphate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$.				
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$.				
0.2000	3	0.0822	0.0831	+0.0009
0.2000	3	0.0832	0.0833	+0.0001
0.2000	3	0.0826	0.0825	+0.0001
Chrome Alum, $[\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3] \cdot 24\text{H}_2\text{O}$.				
$\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$.				
0.2000	4	0.0807	0.0800	-0.0007
0.2000	4	0.0755	0.0755	0.0000
0.2000	4	0.0780	0.0794	+0.0014
Potassium Alum, $[\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3] \cdot 24\text{H}_2\text{O}$.				
$\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$.				
0.2000	3	0.0915	0.0923	+0.0008
0.2000	2	0.0911	0.0929	+0.0018
0.2000	3	0.0910	0.0915	+0.0015
0.2000	3	0.0915	0.0928	+0.0013

From the results detailed in the above table it is evident that there is no loss other than water during the fusion. Even from aluminium and chromium sulphates which lose their acidic oxide on simple ignition, no sulphur trioxide is volatilised in the presence of sodium tungstate. The water of crystallisation of these sulphates may, therefore, be determined in a remarkably short time and with great accuracy with the use of this flux, and the advantage to be derived is obvious and needs no particular comment.

In the case of an acidic sulphate the entire amount of the acidic oxide will be retained by the tungstate, and the water of constitution as well as the water of crystallisation will be evolved.

The extension of the use of this flux to the estimation of water in salts other than sulphates is, for lack of time, left to some future date.—*American Journal of Science*, xxxvi., p. 401.

A CORRELATION OF THE ELASTIC BEHAVIOUR OF METALS WITH CERTAIN OF THEIR PHYSICAL CONSTANTS.*

By JOHN JOHNSTON.

(Concluded from p. 163).

ACCORDING to Beilby (*loc. cit.*), the process of deformation is always accompanied by a partial transformation of the metal to an "amorphous" form (see Note 14), which acts as a cementing material for the untransformed grains. According to Faust and Tammann (*Zeit. Phys. Chem.*, 1911, lxxv., 108), on the other hand, the change of properties on deformation is parallel to the production of smaller crystallites. Whichever be the correct interpretation—if, indeed, these views are mutually exclusive (see *brox.*)—the fact remains that deformation of a metal is accompanied by changes in its properties. These changes are such that they would be rather difficult to account for reasonably, except on the very simple supposition than an actual melting has occurred.

Against this view it might be urged that the pressures required to cause the metals to melt about the ordinary temperature are so great that they are unlikely to occur in practice. But this objection loses weight when it is remembered that the brunt of any strain, to which a crystalline mass is subjected, is borne by a small number of crystals at any one time. When these crystals give way, others take up the strain, and so on. In this way, relatively very small total forces could produce very considerable pressures locally, pressures sufficient to cause melting at those points. This process would be like the method of tearing a pack of cards, which consists in holding them in such a way that the force comes on only one card at a time.

This point of view accounts plausibly for other aspects of the behaviour of metals—for instance, the "hardening" of metals and the increase of strength following upon deformation; but before proceeding to discuss this, it seems advisable to outline a mechanical picture of the probable mode of action of unequal pressure upon a metal.

Poynting (*Phil. Mag.*, 1881, [5], xii., 32), and also La Chatelier (*Zeit. Phys. Chem.*, 1892, ix., 338) have used this conception of unequal pressure to account for regelation—the consolidation of a mass of loose snow at 0° into a block of solid ice. The pressure, due to the superincumbent material, lowers the melting-point at the surface of contact of adjacent grains by an amount Δt . The water formed flows out into the interstices of the snow grains, where it is at a pressure of 1 atmosphere but at a temperature of $-\Delta t$, and is in contact with ice at 0°; consequently it freezes again. This process continues until all the interstices are filled up; that is, until a solid block of ice is formed.

Considerations analogous in every respect are applicable to systems of solid grains in contact with water or an aqueous solution. In such cases pressure acting only on the solid increases its solubility, and renders the solutions supersaturated as soon as they are out of contact with the compressed solid. Le Chatelier accounts in this way for the consolidation of natural beds of rock-salt, gypsum, calcium carbonate, &c., and he showed by direct experiment that consolidation could be produced in this way.

The behaviour of metals under the action of a differential compression we conceive to be identical with that pictured above for ice. Namely, that metal melts wherever the pressure reaches the appropriate value, flows into the interstices where the pressure is smaller, and solidifies again, with the formation in general of very small crystals, by reason of the exceedingly rapid rate of re-crystallisation.

The effects of unequal pressure are analogous to those produced by a shearing stress; or, perhaps, one should say rather that the effects of a shearing stress are those

produced by what we have termed unequal pressure. Now a longitudinal tensile stress can always be resolved into a uniform dilatation and a shearing stress, just as a longitudinal compressive stress can be regarded as composed of a uniform compression and a shearing stress. Hence the conception of unequal pressure, and its effect on the melting-point of a crystalline substance, is equally applicable to all permanent deformations, whether produced by compression or by tension.

When pictured in the way outlined in the above paragraphs, it is obvious that one might expect a parallelism between the ϕ values and certain of the mechanical properties; in all cases, namely, in which the property in question—for instance, tensile strength or flow pressure—implies in any way a permanent deformation of the material, the latter being presumed always to be a manifestation or a real melting produced wherever the stress reaches the appropriate value. In regard to the purely elastic properties—those, e.g., compressibility, which imply no permanent change in the material—the parallelism can hardly be ascribed to a melting; but it may very well be an expression of the fact that the elastic properties and the ϕ values as calculated in this paper are all functions of some one determining factor. (This question is treated later). But even if this is so, it in no wise detracts from the plausibility of the view that deformation is conditioned by an actual melting; for there is no apparent necessary connection between the modes of action of stresses which produce deformation and of those which do not.

The possibility of accounting in this way for the flow of solids was considered by Tammann (*Ann. Phys.*, 1902, [4], vii., 198; "Krystallisieren und Schmelzen," Leipzig, 1903, p. 173), but summarily rejected by him on what appear to the writer to be insufficient grounds. In the first place he doubts the thermodynamic admissibility of the derivation of the formula for the lowering of equilibrium temperature by unequal pressure. In the second place, in his experimental work he was unable to detect any discontinuity in the rate of flow at the pressure indicated by the formula as the melting pressure at that particular temperature. To reason from this lack of discontinuity that the effect of unequal pressure upon the melting-point is illusory might be justifiable if Tammann had been dealing with a single crystal; but dealing as he was with a conglomerate of crystals, flow began whenever the pressure on any one of them exceeded the melting pressure under the particular conditions. Indeed, the behaviour of ice in this respect is precisely similar to that of the metals—a fact specifically noted by Tammann himself—the only difference being that the absolute values of the pressure are lower than for the common metals.

Tammann concludes (*loc. cit.*):—"From the work on the velocity of flow of crystalline substances it follows that the flow is not conditioned by a previous melting, but that the plasticity, the reciprocal of the viscosity, is a property characteristic of the substance." In order to account for the fact that the velocity of flow, and hence the "plasticity," of ice increases very considerably with the pressure, it must be assumed that its viscosity diminishes greatly with pressure. This assumption may hold, for water at low temperatures and low pressures is an exception to the general rule that the viscosity of liquids is increased by pressure (R. Cohen. *Ann. Phys.*, 1892, xlv., 665; Hauser, *Ibid.*, 1901, v., 597); to the writer, nevertheless, it seems less forced to account for the flow by the aid of the argument advanced in this paper, namely, that flow is the result of a partial melting. On this basis we can readily see why increased pressure, which causes more ice to melt, and hence increases the amount of water present, should increase the plasticity. Moreover, so far as the writer has been able to ascertain, this explanation conflicts with none of the recorded observations on the flow either of ice or of any other substance. Indeed, it receives direct confirmation from some recently published work of Hess on the plasticity of ice (*Ann. Phys.*, 1911, xxxvi., 449); he

* From the *Journal of the American Chemical Society*, vol. xxxiv., No. 6.

found, as Tammann previously had also observed, that at a given temperature a considerable movement of the plunger takes place under a pressure much lower than that deduced thermodynamically (on the assumption that the pressure acts *equally* on both the ice and the water produced by the melting), and presents indisputable evidence that the ice in these circumstances had actually melted.

The mode of action outlined in this paper, besides accounting plausibly for the magnitude of some of the mechanical properties of metals, can also be adduced to explain observations on the structure of metal which has "flowed," or has been subjected to deformation of any kind. The process of "flow," or of deformation, of a metal is always accompanied, as we have seen, by a number of changes, among others by a "hardening" of the metal; this term is used to denote an increased resistance to stress, and is in one sense unfortunately chosen, for Faust and Tammann (*Zeit. Phys. Chem.*, 1911, lxxv., 118) have shown that in some cases the "hardness," as measured by the sclerometer, is not affected by the process of "hardening." Faust and Tammann, by microscopic observation of the specimens, were able to determine with a precision of about 1 per cent the pressure or tension required to produce the first permanent deformation of a number of metals, and found that this lower elastic limit is the same for pressure as for tension. Further, slow increase of pressure above the lower elastic limit causes this limit to recede to higher pressures, until finally an upper elastic limit, the flow pressure, is reached. This, again, shows that increase of pressure produces an increased rigidity of the metal, which is in accordance with the idea, first enunciated by Beilby, that the change in properties of metals on hammering, rolling, &c., is a direct consequence of the deformation which occurs during the process.

Now, these facts accord well with the argument of the present paper; for, exactly as in the case of the consolidation of loose snow to a block of ice, as soon as the stress reaches an appropriate value (the lower elastic limit), melting and flow into the interstitial spaces take place, with immediately subsequent re-crystallisation; this process continues until this flow is no longer possible (the upper elastic limit), whereupon increased stress produces rupture of the material. Now, the actual process of flow diminishes the volume of the spaces into which flow is possible, and to this extent diminishes the inequality of pressure acting on liquid and solid; hence it requires progressively higher pressures absolutely (though at the same temperature the same *excess* of pressure on the solid) to produce flow; in other words, the rigidity of the material is increased.

A phenomenon analogous in every respect to that observed by Faust and Tammann has been recorded by Bridgman (*Phys. Rev.*, 1912, xxiv., 1) in some very recent work on the collapse of thick walled cylinders under high hydrostatic pressure. Bridgman found, namely, that with every successive application of pressure, yield is not resumed until the previous pressure maximum has been reached or exceeded; this behaviour is just what we should expect if flow is conditioned by a true melting.

It is important to observe, in passing, that uniform (hydrostatic) pressure is without *permanent* effect on the properties of metals. Thus, Faust and Tammann found that the elastic limit of metal which had been subjected to high hydrostatic pressure remains unchanged; while, as regards the physical properties (density, &c.), it is generally recognised that the only effect of hydrostatic pressure is a temporary change in these properties, which vanishes again whenever the pressure is removed. In all discussions of the effect of pressure therefore it is essential that we distinguish carefully between uniform and non-uniform compression, since their effects are so dissimilar.

It is a well known fact that the resistance to flow of eutectics (which are always fine grained) is always greater than that of their components (see Note 15); further, that the varieties of steel possessing the greatest tensile strength (e.g., vanadium steels) are very fine grained. From the

standpoint adopted in this paper one might reason that such metals are strong *because* they are fine grained; hence, if we wish to make a steel of high tensile strength, we should endeavour to obtain a very fine grained structure, producing this by whatever means (addition of foreign material, heat treatment, or mechanical treatment) may be found suitable for this purpose.

It was noted above that the deformation of metals is accompanied by the appearance of an "amorphous" phase, according to Beilby; by the production of smaller crystallites, according to Faust and Tammann. Neither author speaks definitely of the mode in which the change takes place, nor do they, as far as one can judge, consider it as a manifestation of real melting, with immediately subsequent re-solidification. When looked at in this way the divergence between their points of view disappears. For, as is well known, the size attained by a crystal depends, *ceteris paribus*, on its rate of formation; so that Beilby, with presumably a relatively rapid rate of re-crystallisation, obtained in his flowed metal crystals so small that the metal was apparently "amorphous"; Faust and Tammann, on the other hand, using a totally different method in which the rate of re-crystallisation was presumably not so great, obtained relatively larger crystal particles.

A point worth mentioning in this connection is this, that the appearance of the cut and polished surface of a metal is not necessarily an altogether fair criterion of the structure of the massive metal. For, as Beilby has demonstrated conclusively, the process of polishing (and obviously of cutting also) is the result of flow; while in accordance with the viewpoint presented in this paper, flow is the result of a partial melting. Therefore, it is a safe assertion that between the apparent structure of the polished surface and the actual structure of the massive metal, there must always be some differences, which may be so large that examination of the surface only would lead to totally misleading conclusions with regard to the structure of the massive metal.

Kurnakov and Zhemzhuzhny (*loc. cit.*) made parallel measurements of the electrical conductivity and flow pressure of series of binary alloys, and found that for given binary systems minimum conductivity and maximum flow pressure occur at the same composition. This exemplifies the general rule that the conductivity of an alloy is less than that of its component metals. Moreover, the conductivity of a metal generally decreases when the metal undergoes deformation (e.g., drawing to wire, hammering, or rolling). Now, if we interpret these facts with the aid of the idea that the specific conductivity of a given material diminishes progressively, other things being equal, with the size of the component particles—an idea which is substantially correct for powdered metals—we find them to be in complete harmony with the conclusion reached on other grounds, namely, that the size of grain of alloys or of metal which has been deformed is less than that of the pure annealed metals.

Summary and Conclusion.

In the foregoing pages we have discussed the idea that the "flow," or permanent distortion, of metals is conditioned by a real melting, not of the whole mass of metal at any one instant, but of successive groups of particles (namely, those on which the brunt of the strain momentarily falls); and have shown how this idea serves to correlate some properties of metals which at first sight would appear to bear no relation to each other. It leads, namely, to the fact that there is a parallelism between all the elastic properties of metals for which quantitative measurements have been made and the pressure—assumed to act on the solid phase, but not, or not to the same extent, on the liquid phase—which is required to lower the melting-point to ordinary temperature. This pressure is a function of the melting-point, latent heat of melting, and density at the melting-point of the metal; hence, if these quantities are known for any substance, we can predict

the relative order of magnitude of any of its properties which imply deformation of the material.

The same mode of reasoning is equally valid for any crystalline substance, and could be applied to all salts (including silicates and other geologically important substances) if the necessary data were available. At the present time, values of the latent heat of melting are few and far between, so that no general discussion of this part of the subject is practicable now.

The equation discussed in this paper cannot be applied to glasses; for since they are merely supercooled liquids, the value of Q is zero and hence dT/dP is infinite. But this is not so contradictory as at first sight it may seem; for glasses behave as liquids of exceedingly high viscosity, provided always that, conformably with this high degree of viscosity, sufficient time be allowed for the motion to take place.

In conclusion, let us give a brief indication of a connection between the relations discussed in this paper and the conception of "molecular vibration frequency," a conception which has been very fruitful in the hands of Nernst and Lindemann (see Note 16), Grüneisen (*Ber. Phys. Ges.*, 1911, 426, 591), and others. It has been established, namely, that a large number of apparently diverse physical properties of a substance—melting-point, specific heats, coefficients of thermal expansion and compressibility, electrical resistance—may be considered to be functions of a characteristic quantity, the molecular "vibration frequency" (see Note 17).

Expressions containing this quantity have been derived by means of which the actually observed variation with temperature of certain of the above properties can be reproduced with remarkable accuracy. Now the flow pressure ϕ at the temperature t is determined by a complicated expression, the value of which depends upon t , T_1 (the ordinary melting-point), L (the heat of melting at T_1), V (the specific volume at T_1), and upon the variation of L and V with pressure and temperature; that is, for any particular substance, ϕ depends upon the above constant quantities and upon the specific heats and coefficients of thermal expansion and of compressibility; each of these quantities is some function of the "vibration frequency," consequently the flow pressure ϕ is also a function of this same characteristic parameter.

In view of the state of our knowledge (at the best, very approximate only at the present time) of the experimental data and of certain of the relations involved, it seems premature to endeavour to deduce a definite mathematical relation between them ϕ and the frequency, or even to determine the exact form of the function. The existence of such a relationship accounts simply for the parallelism between the calculated ϕ values (of Table I.) and the mechanical properties of metals brought together in Table II.; for all of these quantities are functions of the vibration frequency, a fact which indicates that all the mechanical properties of metals will be found to be periodic functions of their atomic weights, since the vibration frequency itself is doubtless such a periodic function.

Notes.

14. Beilby here uses the term "amorphous" to denote "a heterogeneous assemblage of molecules."

15. This was demonstrated conclusively by Kurnakov and Zhemzhuzhny (*Zeit. Anorg. Chem.*, 1908, lx., 1; 1909, lxiv., 149), who present results—in part from the literature, in part original—for a large number of alloys (and also for some pairs of organic substances) which demonstrate this fact. It has been further confirmed by Tammann, who recently (*Nachr. Ges. Wiss. Göttingen*, 1911, p. 181) described experiments with a few alloys, carried out in quite a different way, from which he draws the conclusions that this increased strength is a direct consequence of the fact that the alloys are finer grained than their components but offers no explanation as to why a fine grained

conglomerate should be stronger than one composed of coarser particles); further, that the increased strength of metals which have been chilled is a direct consequence of the decreased size of the grains produced by rapid cooling of the melt.

16. This work has been published in a series of recent papers which have appeared in *Sitz. Akad. Wiss. Berlin*, *Ann. Phys. Zeit. Elektrochem.*, and *Phys. Zeit.*

17. For a discussion of the exact significance of this quantity, the reader may be referred, in addition to the papers cited above, to recent papers by Einstein in *Ann. Phys.*

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 26, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Nature of the Tubes in Marsupial Enamel and Bearing upon Enamel Development." By J. H. MUMMERY.

"Oxidation of Thiosulphate by certain Bacteria in Pure Culture." By W. T. LOCKETT.

In the course of investigations on the oxidation of thiosulphate on bacterial sewage filters, it was found that the oxidation was due largely to the presence of living organisms. Experiments were undertaken with a view to the isolation of the organism or organisms capable of bringing about this oxidation.

Active solutions on plating out with gelatin (G.P.B.) and agar (A.P.B.) showed approximately 100 organisms per cc. Several of the more predominating types of organisms in pure culture, isolated from the above plates, were unable to bring about the oxidation of thiosulphate.

Subsequently, it was observed that a bacteriological slide made of a loopful of an active solution showed proportionately a greater number of organisms per cc. than was indicated by the gelatin and agar plates of the same solutions. Further, the microscopic appearance of these—consisting mainly of one particular type—was very different from that of the organisms previously subcultured.

All attempts to grow the particular and characteristic organism on the usual media, e.g., nutrient gelatin and nutrient agar, failed. Ultimately it was found on plating an active solution on a solid gelatin medium, without bouillon, but containing ammonium sulphate and thiosulphate, that a great number of minute, slow-growing, circular, non-liquefying, bluish white colonies were obtained.

Plates made with such a medium showed that active solutions contained 100 to 1000 times more organisms per cc. than was shown on gelatin and agar.

The organism isolated as above on inoculation into a solution of thiosulphate, containing ammonium sulphate and a small quantity of free tartaric acid, was found capable of oxidising thiosulphate to sulphate in the course of two to three weeks' incubation at 20° C.

Further work is in progress relating to the morphology and classification of the organism which is apparently one hitherto unknown.

"Production of Anthocyanins and Anthocyanidins." By A. E. EVEREST.

The question of the production of Anthocyan pigments from the yellow pigments of the flavone and flavonol class is discussed.

Evidence is brought forward to show that the Anthocyan pigments must be regarded as reduction products of

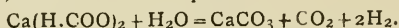
flavone or flavonol derivatives, and that they are readily produced as glucosides from the glucosides of the yellow compounds without intermediate hydrolysis.

"Variations in the Growth of Adult Mammalian Tissue in Autogenous and Homogeneous Plasma." By A. J. WALTON.

"(1) The Decomposition of Formates by *B. coli communis*; (2) The Enzymes which are concerned in the Decomposition of Glucose and Mannitol by *B. coli communis*." By E. C. GREY.

(1) The object of the investigation was to determine how an organism which produced only a trace of gas from a formate and no gas from glucose when acting on these separately was able to produce gas abundantly from a mixture of the two.

An artificially selected strain of *B. coli communis* which now produced no gas from glucose was made to act upon a mixture of calcium formate and glucose. The CO_2 evolved was measured. From this the CO_2 equivalent to the acids produced from the sugar was deducted. The difference represents CO_2 from formate, but must be multiplied by two, since only half the CO_2 produced is evolved, as seen from the equation—



The results obtained indicate that the addition of glucose increased the decomposition of formate at least twenty-fold.

The explanation of the cases where CO_2 is not produced (formate alone, glucose alone) is that decomposition is inhibited readily by excess of acid or of alkali. But with the mixture the conditions are ideal for maintaining neutrality. The acid produced from the sugar neutralises the alkali produced from the formate. The reactions are thus mutually helpful, and, moreover, either regulates the velocity of the other.

The application of the results is suggested in the use of formates in certain cases in the place of alkali for maintaining the neutrality of media. The method described would be of value also (1) As a surer test of the capability of an organism to decompose formates; (2) As a criterion whether a strain apparently producing no gas from glucose may have been recently derived from a gas-producing strain.

(2) The work aims at determining the number of separate enzymes concerned in the decomposition of glucose and mannitol by *B. coli communis*.

The method consists of a comparison of the ratios in which the various products are formed by the normal organism with the ratios in which they are formed by artificially derived strains.

According as the ratios are constant or vary it may be deduced that the products arise by the same or different enzymes.

The main products are lactic acid, alcoholic acetic acid, and formic acid or its cleavage products ($\text{CO}_2 + \text{H}_2$).

The only ratio found for both glucose and mannitol which proved constant on selection was—

$$\frac{\text{Alcohol} + \text{acetic acid}}{\text{Formic acid} \times 2} = \text{unity}.$$

From this it is concluded—(1) Alcohol and acetic acid are derived from a common parent substance, probably acetaldehyde; (2) This substance is formed by an enzyme which also produces formic acid.

This parent substance (intermediate substance B) is regarded as being produced together with formic acid from a hypothetical (intermediate substance A) which is itself an isomer of lactic acid.

The essential differences between the proportions of the products arising from glucose as compared to mannitol may be shown to be conditioned by the extra hydrogen in mannitol. These considerations have been embodied in a scheme to represent on a common basis the decomposition by *B. coli communis* of glucose and mannitol.

Evidence has also been adduced indicating that the process of artificial selection herein referred to has led to the production of an organism deficient in reductase.

"Description of a Strain of *Trypanosoma brucei* from Zululand. Part I. Morphology. Part II. Susceptibility of Animals. Part III. Development in *Glossina morsitans*." By Surg.-General Sir D. BRUCE, F.R.S., Major A. E. HAMERTON, Captain D. P. WATSON, and Lady BRUCE.

"The *Trypanosoma* causing Disease in Man in Nyasaland. Part III. Development in *Glossina morsitans*." By Surg.-General Sir D. BRUCE, F.R.S., Major A. E. HAMERTON, Captain D. P. WATSON, and Lady BRUCE.

CHEMICAL SOCIETY.

Ordinary Meeting, March 19, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President,
in the Chair.

(Concluded from p. 166).

83. "The System Silver—Silver Sulphide." By CRELLYN COLGRAVE BISSETT.

The above system has been investigated both by thermal and by microscopic methods. From the results of the investigation it was concluded that:—(1) Silver and silver sulphide are only partially miscible in the liquid state. All alloys having an average composition between approximately 17 and 94 per cent of sulphide separate into two layers on being melted, and freeze at a constant temperature of 903° .

2. Silver and silver sulphide form a eutectic containing approximately 99 per cent of sulphide. The freezing-point of the eutectic was found to be 804° .

3. Silver and silver sulphide probably form solid solutions to some extent.

84. "The Action of Sulphur on Amines. Part II. Aniline." By HERBERT HENRY HODGSON and ALFRED GILBERT DIX.

The authors have studied the action of sulphur on aniline in the presence of its hydrochloride or hydrochloric acid. It is found that trithioaniline is produced in quantitative yield, and the previous discrepancies of other authors are to be explained by secondary actions between the trithioaniline, aniline, and sulphur. Although the free base itself could only be obtained in a resinous condition, the sulphate, hydrochloride, and oxalate have been prepared, together with the benzoyl derivative. The wool dye-stuffs obtained by diazotising the sulphate and combining with the usual components were found to be exceptionally fast to ordinary agents, and particularly so to milling. Iodine had the same influence as hydrochloric acid on the course of the reaction. On reduction the trithioaniline gives a dithioaniline, but the poor yield has led to an investigation of the mechanism of the reduction. Anomalies noticed when trithioaniline is condensed with *m*-nitrobenzaldehyde, and also when diazotised and coupled with 8-naphthol, seem to indicate that one of the sulphur atoms is only loosely combined.

85. "Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part VI. The Optical Rotatory Powers of Methyl-tert.-butyl-, Methylbenzyl-, Methylphenylethyl-, and Methyl- α -naphthylcarbinols." By ROBERT HOWSON PICKARD and JOSEPH KENYON. (This paper corresponds in part with the preliminary note published in *Proc.*, 1912, xxviii., 42).

The preparation of the optically active forms of these carbinols was described.

1-Methyl- α -naphthylcarbinol (m. p. 47°), when supercooled at the temperature of the laboratory, exhibits anomalous rotatory dispersion.

86. "Salts which contain Two Solvents of Crystallisation." By JAMES ERNEST MARSH.

When the salt $\text{KHgI}_3 \cdot \text{H}_2\text{O}$ is added to methyl carbonate,

the clear yellow crystals crumble to a nearly colourless powder. On warming, all passes into solution, and on cooling the salt $\text{KHgI}_3 \cdot \text{H}_2\text{O} \cdot 3\text{Me}_2\text{CO}_3$ crystallises out. The ammonium salt $\text{NH}_4\text{HgI}_3 \cdot \text{H}_2\text{O} \cdot 2\text{Me}_2\text{CO}_3$ crystallises well. The rubidium salt $\text{RbHgI}_3 \cdot \text{H}_2\text{O} \cdot 2\text{Me}_2\text{CO}_3$ is also crystalline, but nearly insoluble in the solvent. A sodium silver iodide with water and methyl carbonate of crystallisation has also been obtained.

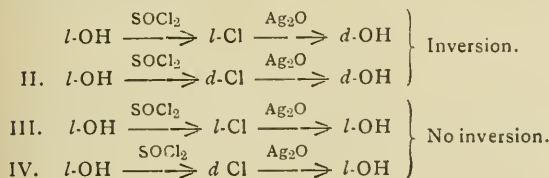
87. "Menthyl Esters of Chloroacetic, Methoxyacetic, and Methylalinoacetic Acids." By PERCY FARADAY FRANKLAND and FRED BARROW.

These compounds have been prepared by the authors in connection with their search for an optically active acid chloride which would be easily accessible and not liable to racemisation.

Owing to the great stability of the ester-grouping in menthyl chloroacetate, the authors find the latter to be a very convenient optically active compound from which to obtain derivatives by the interaction of the halogen-atom and other groups. Thus menthyl menthoxyacetate and menthyl methylalinoacetate were obtained by the action of sodium menthoxide and methylaniline respectively on menthyl chloroacetate. (Compare also the use made by P. F. Frankland and H. H. O'Sullivan of menthyl chloroacetate and menthoxyacetic acid, *Trans.*, 1911, xcix., 2325; 1912, ci., 287).

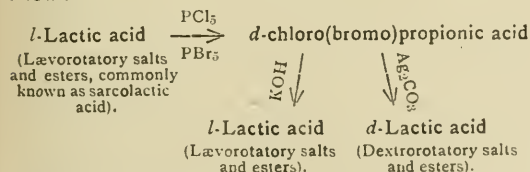
88. "The Action of Thionyl Chloride on Lactic Acid and on Ethyl Lactate." By PERCY FARADAY FRANKLAND and WILLIAM EDWARD GARNER.

The authors direct attention to the apparent regularity in the action of thionyl chloride and silver oxide on optically active hydroxy-compounds. Four possibilities present themselves:—

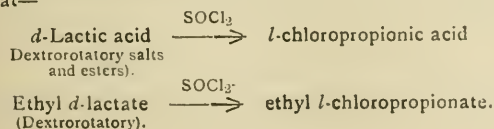


Only six hydroxy-compounds have hitherto been investigated in their relation to this pair of reagents, and in every case an inversion is effected, the transformation taking place according to scheme I. in the case of phenylglycolic acid (mandelic acid), α -hydroxy- α -phenylpropionic acid (atrolactic acid), β -hydroxy- β -phenylpropionic acid, and phenylmethylcarbinol, and according to scheme II. in the case of malic acid and α -hydroxy- β -phenylpropionic acid, although for the latter compound the data are incomplete and somewhat obscure. Hitherto no transformations according to schemes III. and IV. have been observed.

The authors have completed the data bearing on lactic acid, for which the following transformations are already known:—



By the action of thionyl chloride the authors have found that—

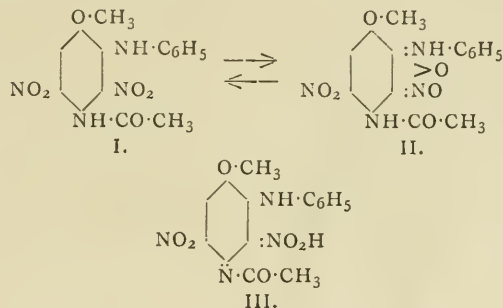


The transformations of lactic acid are, therefore, similar to those of malic acid, and take place according to scheme II. above.

A number of intermediate compounds were encountered in the action of thionyl chloride on the lactic acid and its ester. Thus, from the feebly active *d*-lactic acid (dextrorotatory salts and ester) employed there were obtained chlorosulphinyl-lactic chloride (very strong dextrorotation), chloropropionyl chloride (feeble dextrorotation), chloropropionic acid (lævorotation), ethyl chloropropionate (lævorotation), chloropropionyl-lactic chloride (dextrorotation), chloropropionyl-lactic acid (dextrorotation), ethyl chlorosulphinyl-lactate (very strong dextrorotation), and ethyl thionyl-lactate (very strong dextrorotation).

89. "Synthesis with Phenol Derivatives containing a Mobile Nitro-group. Part VI. Substituted Alkyl- and Aryl-phenylamines; Colour in Relation to Tautomerism." By RAPHAEL MELDOLA and WILLIAM FRANCIS HOLLELY.

The authors have studied the action of primary and secondary amines on the 2:3:5 trinitroanisidine of Reverdin, and have obtained a series of alkyl- and aryl-phenylamine derivatives, all of which result from the replacement of the 2-nitro-group by the amine residue. Tertiary amines have no action. The compound obtained by the action of aniline, 3:5-dinitro-2-phenylaminoacetophenonide, exists in two differently coloured tautomeric forms which are interconvertible, and to which the authors assign the formulæ:—



One of these modifications is ochreous and the other red, the latter being regarded as an inner salt (II.) and the former as having the normal constitution (I.). Both forms dissolve in alkali with a yellow colour; the authors give reasons for believing that in alkaline solution configuration III. exists, this form reverting at once to I. when precipitated by acids.

90. "A Formula by means of which the Molecular Volume at the Boiling-point may be Calculated." By GERVAISE LE BAS.

In an extended study of molecular volumes, it was found necessary to calculate some of the values at the boiling-point, and the following formula has been found suitable for this purpose:—

$$\frac{273}{\text{B. p.}} = \left\{ 1 - c \left(\frac{d_t}{d_0} - 1 \right) \right\}.$$

The only data necessary are the density at 0° and the boiling-point.

The value of *c* is given in Table I., the data being those of Thorpe.

It is found that by means of the above formula the volumes of compounds of a similar order of complexity can be calculated to within 1 per cent.

Example.— GeCl_4 , d_{18} 1.887 (Winkler), b. p. 86.0°, $\frac{273}{T} = 0.771$, $\frac{d_0}{d_t} = 0.46 \times 0.229 = 1.1053$, $d_{\text{b.p.}} = \frac{1.887}{1.105} = 1.708$. M.W. = 213.8; M.V. 124.6.

Observed, C 14.8, Si 32, Ge [36.2], Sn 42.3, Ti [35.7].

The formula can be used indifferently for inorganic and organic compounds, but the value of *c* in the latter varies

TABLE I.—Table of Values (Inorganic Compounds).

Compound.	B. p.	d_0 .	$d_{b.p.}$	c .	M.V. calc.	M.V. obs.	Per cent error.
$\text{S}_2\text{O}_5\text{Cl}_2$	139.6	1.85846	1.60610	0.460	135.5	135.5	± 0.0
$\text{SO}_2\text{Cl}\cdot\text{OH}$	155.3	1.78474	1.54874	0.420	75.5	75.05	± 0.7
SO_2Cl_2	70.0	1.70814	1.56025	0.462	86.3	86.3	± 0.0
AsCl_3	130.2	2.20500	1.91813	0.447	95.1	94.37	+0.76
AsF_3	60.4	2.6659	2.4497	0.490	53.6	53.84	-0.44
VOCl_3	127.2	1.86534	1.63073	0.452	106.5	106.2	+0.3
POBrCl_2	137.6	2.12065	1.83844	0.458	107.5	107.4	+0.1
PSCl_3	125.1	1.66820	1.45599	0.455	116.3	116.1	+0.2
POCl_3	107.2	1.71163	1.50967	0.474	101.0	101.4	-0.4
TiCl_4	136.4	1.76041	1.52223	0.460	124.5	124.5	± 0.0
SiCl_4	57.6	1.52408	1.40294	0.500	120.2	120.8	-0.5
N_2O_4	21.6	1.49030	1.43958	0.473	64.0	63.9	± 0.0
Mean value				0.463			

TABLE II.—Cyclic Compounds.

Compounds.	M. p. or α .	B. p.	d_1 . α° or m. p.	d_1 . T=B. p.	c .	M.V. calc.	M. V. obs.	Per cent error.
C_6H_6 (benzene)	6.0°	80°	0.8940	0.8133	0.470	95.7	96.0	-0.03
$\text{C}_4\text{H}_4\text{S}$ (thiophen)	0.0	84	1.0884	0.9874	0.434	85.5	85.0	+0.6
C_{10}H_8 (naphthalene)	79.2	217	0.9777	0.8674	0.456	147.3	147.2	± 0.0
$\text{C}_{10}\text{H}_{14}$ (hexahydronaphthalene)	0.0	200	0.9419	0.7809	0.487	170.0	171.2	-0.7
$\text{C}_{14}\text{H}_{10}$ (phenanthrene)	100.5	340	1.0630	0.9073	0.440	197.8	195.2	+1.3
$\text{C}_5\text{H}_5\text{N}$ (pyridine)	0.0	115	1.0033	0.8826	0.462	89.3	89.3	± 0.0
$\text{C}_9\text{H}_7\text{N}$ (quinoline)	0.0	234	1.1081	0.9211	0.439	141.1	140.0	+0.8
Mean value					0.460			

somewhat as the compounds vary greatly in complexity and the chains lengthen.

The value of c for organic cyclic compounds without side-chains is similar to the above. (See Table II.).

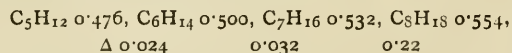
The results of calculation show very fair agreement with observation, and thus giving a fairly trustworthy method for the calculation of unknown values.

Example.—Hydrindene, C_9H_{10} : d_5 0.957, b. p. 176° , $c=46$, M.V. 144.0. $\Sigma nVa = (4 \times 9 + 10)3.7 = 46 \times 3.7 = 170.2$, $\Delta = -26.2$ for ring. Contraction for 1 six-membered ring + 1 five-membered ring = $-15 - 11.5 = -26.5$.

Acenaphthene, C_{12}H_8 .—The value of c for phenanthrene is 0.440. For acenaphthene, d_{103} 1.030, m. p. 103° , b. p. 277° . V_m 166.6, ΣnVa 207.2, $\Delta = -40.6$. Contraction for 2 six-membered rings + 1 five-membered ring = $-30.0 - 11.5 = -41.5$.

The only difficulty is met with in open-chain organic compounds. For compounds like chloroform, carbon tetrachloride, and trichloromethane, the value of c mentioned above (0.460) may suffice.

c , in general, increases by 0.024 for every addition of CH_2 in open-chain compounds, thus:—



When considering an unknown value for a certain compound, it is usually possible to find an analogous compound from which c may be calculated, for example, cymene, $\text{C}_{10}\text{H}_{14}$, for the terpenes (menthane), $\text{C}_{10}\text{H}_{16}$, methyl succinate for methyl maleate or fumarate, propionitrile for ethyl carbamate, and ethyl nitroethane for ethyl nitrite.

91. "A Study of the Constitution of Nitrogen and Phosphorus Oxides and some of their Derivatives by means of Molecular Volumes." By GERVAISE LE BAS.

A study has been made of the above compounds by means of a new theory of molecular volumes, based on the original one of Kopp, or at least from his point of view. It recognises an additive principle, which is shown by the use of a system of atomic volumes, as follows:— $\text{C}=14.8$, $\text{H}=3.7$, $\text{O}=7.4-11.0$, according to circumstances, $\text{S}=22.0$ and 25.6 , $\text{N}=15.6$, $\text{P}=27.0$. A number of constitutive features are also recognised. As

a consequence, the constitutions of some of the above compounds are considered to be different from those usually accepted.

MISCELLANEOUS.

Method of Determining Glucinum.—André Kling and E. Gelin.—To determine glucinum mixed with oxides of aluminium and iron the hydroxides are first precipitated with ammonium chloride and ammonia, treated with nitric acid, and cautiously calcined. The residue is converted into acetates by means of pure acetic acid, and the mixed acetates are sublimed in a rarefied atmosphere containing acetic acid vapours. The basic acetate of glucinum is totally volatilised and is deposited on the cold parts of the glass tube in which the operation is carried out, while the basic acetates of aluminium and iron remain behind.—*Bull. de la Soc. Chim., de France*, No. 3, 1914.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 6th inst., The Duke of Northumberland, President, in the Chair. Miss A. R. Atkinson, Lady Esmonde, Mrs. H. J. F. Simson, and Mr. F. W. Goodenough were elected Members. The Chairman announced that the septennial award under the Acton Endowment had this year been made to Prof. C. S. Sherrington, Waynflete Professor of Physiology in the University of Oxford, for his important work entitled "The Integrative Action of the Nervous System," being a synopsis of his elaborate paper published in the *Philosophical Transactions of the Royal Society* on Experiments in Examination of the Peripheral Distribution of the Fibres of the Posterior Roots of some Spinal Nerves. Previous Actonian Awards have been made to Sir George Stokes, Miss Agnes M. Clerke, Sir William and Lady Huggins, and Mme. Curie, for achievements in the field of physical science. Prof. Sherrington is the first investigator in Experimental Biology to receive this distinction for the third of a century.

MEETINGS FOR THE WEEK.

WEDNESDAY, 15th.—Microscopical, 8. "The Insect Pests of Wheat Crops," by F. Enock.

THE CHEMICAL NEWS.

VOL. CIX., No. 2838.

THE GENERAL BEHAVIOUR OF OPTICALLY ACTIVE COMPOUNDS AS REGARDS THE DEPENDENCE OF ROTATION ON TEMPERATURE, DILUTION, NATURE OF SOLVENT, AND WAVE-LENGTH OF LIGHT.*

By T. S. PATTERSON, D.Sc., Ph.D.

SOME twenty years ago the general opinion in regard to the influence of temperature on the rotation of an optically active substance probably was that the rotation, as in the case of a substance like ethyl tartrate, tended towards a constant value at higher temperatures, that the temperature rotation curve became asymptotic to the axis of temperature. In 1896, however, it was shown by Frankland and Wharton (*Trans. Chem. Soc.*, 1896, lxix., 1587) in the case of ethyl dibenzoyl tartrate that a minimum rotation could exist, and some years later Winther (*Zeit. Phys. Chem.*, 1902, xli., 176), in an investigation connected with rotation-dispersion, fitted a parabolic expression to a number of temperature-rotation curves and made the assumption that since the parabola has a maximum, therefore the rotation of these substances should also pass through a maximum value. Somewhat later still the present writer showed that this maximum actually exists (*Trans. Chem. Soc.*, 1908, xciii., 1843), although at a different temperature from that deduced by Winther, and showed also that the maximum, instead of occurring at a constant temperature in a series of homologous compounds, or on dilution of an active substance with an indifferent solvent, moves gradually through a range of temperature. Thus, in nitrobenzene, for instance, the maximum rotation of ethyl tartrate, which occurs at a temperature of about 175°, moves rapidly towards a lower value as the solution becomes more dilute, the rotation, at the same time, becoming gradually greater. It thus becomes immediately clear why the rotation of a dilute solution of ethyl tartrate in nitrobenzene diminishes with rise of temperature, whilst the rotation of the ester itself and of its more concentrated solutions in nitrobenzene increases on heating; in the former case the ordinary temperature is on one side of the maximum, whilst in the latter case it is on the other. The temperature coefficients of all solutions of ethyl tartrate in nitrobenzene are less than that for the pure ester; nitrobenzene at the ordinary temperature has a powerful elevating effect on the rotation of this particular active compound. A number of other substances, however, of which acetylene tetrabromide may be taken as the best example, have an opposite effect. These substances have a considerable power to depress the rotation of the ester, and in agreement with this it is found that the temperature coefficient of all solutions made up of ethyl tartrate and that solvent have temperature coefficients which are greater than that of the pure ester. It may therefore be inferred that in these cases the maximum rotation would still persist but would move towards a still higher temperature, which in this particular case has not yet been actually observed. (Such evidence as exists in regard to this question will be found in a paper in the *Trans. Chem. Soc.* for 1913, ciii., 145, especially, perhaps, p. 171).

Further, it has been found that other solvents produce effects of a closely similar kind in such a way that if, for instance, a solution in water and one in nitrobenzene have

one and the same rotation at some given temperature, then the temperature-rotation curves of the two solutions will be closely similar, although the concentrations may be entirely different. Thus the curve for a number of different solvents at various concentrations blend into a diagram remarkably like that for one single solvent at a number of concentrations, and it would seem as if we might almost eliminate from consideration the nature of the inactive solvent and the concentration, since the course of the temperature-rotation curve is apparently defined by the rotation at any given temperature (see Fig. 3, *Trans. Chem. Soc.*, 1908, xciii., 1846). When the influence of a particular solvent appears to be exhausted—that is, when its maximum influence has been reached in a dilute solution—the influence may be taken up, as it were, and carried on by another one more powerful. Thus α -nitronaphthalene, $p = 55$, has approximately the same effect as nitrobenzene, $p = 5$, so that the α -nitronaphthalene at $p = 25$ appears to pick up the influence of the nitrobenzene at that point and carry it farther.

Another matter of interest in connection with the relation between temperature and rotation is the following. It has been found that certain substances, such as ethyl tartrate, show a maximum rotation, whereas some derivatives of that compound, for instance ethyl ditrichloroacetyl tartrate, show on the contrary a temperature of minimum rotation, and a reconciliation of this exactly opposite behaviour must obviously present some difficulty. Possibly, however, the reconciliation may be effected in this way. It is known that the substitution of an alkyl radicle, such as *n*-propyl, *iso*-butyl, &c., for ethyl, in ethyl tartrate, moves the maximum rotation towards a lower temperature, whilst at the same time the actual value of the rotation is increased (*Trans. Chem. Soc.*, 1913, ciii., 148), and it seems reasonable to suppose that the very much greater change involved in the replacement of the hydroxylic hydrogen by the trichloroacetyl group should produce a correspondingly greater shifting of the temperature of maximum rotation. The maximum may, in fact, be shifted out of the region of ordinary temperatures altogether and the portion of the curve for the ditrichloroacetyl derivative may correspond with some part of the graph for ethyl tartrate, a part with which we are unacquainted, only because we are not able at present to investigate the problem over a sufficient range of temperature. An examination of some of the data which have been obtained by various observers in the investigation of certain active substances over a fairly wide range of temperature strongly supports this view, for it is found that not only do maxima and minima exist in different curves, but that in the same curve not infrequently a maximum or a minimum together with a point of inflection may be observable.

No investigation has yet been carried out over a sufficient range of temperature to reveal both a maximum and a minimum. (This question has been fairly fully discussed elsewhere—*Trans. Chem. Soc.*, 1913, ciii., 151).

The temperature-rotation curve of an active compound is thus probably periodic, that is, may show several maxima and minima, and it seems probable that the influence of a solvent is simply to shift the complete curve of the homogeneous substance in one direction or another, but, of course, probably with minor alterations. Thus for ethyl tartrate the influence of nitrobenzene seems to be to shift the whole curve simultaneously towards a lower temperature and a higher rotation.

Rotation Dispersion.—Another very interesting question relates to the position of the maximum rotation for different colours of light. This is a subject which has been thoroughly investigated in only very few cases, but it would appear from the results which have been obtained that the maximum does not necessarily occur at the same temperature for different colours of light. Only two substances have been examined, ethyl tartrate and *n*-propyl tartrate, and in both the maximum rotation moves towards a higher temperature as the wave-length of the light

* Contribution to a General Discussion on "Optical Rotatory Power," held before the Faraday Society, March 27, 1914.

becomes less (*Trans. Chem. Soc.*, 1913, ciii., 165, 166). The temperature-rotation curve for violet light is thus apparently retarded on the temperature-rotation curve for yellow or for red light.

This is chiefly important in connection with what is called rotation dispersion. It is well known, of course, that the rotation of an active substance usually depends on the wave-length of the light used, and it is often stated that the rotation for violet light is greater than that for red. If, on the diagram showing the temperature-rotation curves for different colours of light in the case of ethyl tartrate, a vertical line be drawn through the temperature 160° , it will cut the temperature-rotation curves (*Trans. Chem. Soc.*, 1913, ciii., p. 165, Fig. 7) in the order violet, blue, green, yellow, red, and if these values be plotted on a new diagram relative to wave-length a graph will be obtained which is always, so far as the writer is aware, a curved line. If the line be drawn, however, at a temperature of say, 80° , it would cut the temperature-rotation curves in the order, blue, green, violet, yellow, red, and on plotting these values of rotation against wave-length a dispersion graph would be obtained rising from red to a maximum at blue and descending again to violet. Such a curve is generally said, without any proper reason, to be abnormal. At some wave-length intermediate between the extremes there is a rotation maximum. If now a line be drawn through the temperature -40° the sequence of the rotation values will be the same as at first, but the violet light gives the lowest rotation, a negative rotation being regarded as less than a positive rotation. This is, however, a purely accidental circumstance and is solely due to the fact that the temperature-rotation curves for ethyl tartrate happen to pass through the point of inactivity in the neighbourhood we are considering, otherwise the values for violet would be numerically less than for red. It is quite essential that in discussing rotation-dispersion some method must be devised which shall eliminate the sign of the rotation, and it would seem desirable to designate the dispersion on one sign of the region of intersection of these curves as positive and that on the other as negative.

The rotation-dispersion is often defined as the ratio of the rotations for various colours of light to the rotation for one given colour of light, such as red or yellow, but it has been carefully pointed out by Winther (*Zeit. Phys. Chem.*, 1902, xli., 205) that this is a very unsatisfactory procedure, giving most misleading values for rotation-dispersion as in the case of methyl tartrate. This point has been overlooked quite recently by Armstrong and Walker and by Pope and Winmill. The latter authors have measured the rotation, for three different lines of the spectrum, of derivatives of tetrahydroquinoline, and in regard to the -nitrobenzoyl derivative state that this substance exhibits quite abnormal rotation constants (*Trans. Chem. Soc.*, 1912, ci., 2311), whilst with regard to the 2-nitrotoluene-4-sulphonyl derivative they say (*loc. cit.*, 2316), "The considerable variation of rotatory dispersion of the latter substance with the solvent used is noteworthy."

Armstrong and Walker (*Proc. Roy. Soc.*, 1913, A, lxxviii., 391) comment on what they term the abnormal dispersive power of these substances, and remark, "It is obvious that a special explanation is required to account for the peculiar behaviour of the two compounds mentioned." The rotatory dispersive power of these substances is, however, not more abnormal than is that of any of the other compounds examined by Pope and Winmill. The explanation, in the first case at least, is in fact purely arithmetical, the cause of any anomaly that exists being identical with that discussed by Winther in the case of methyl tartrate, already referred to, namely, that in certain of the solvents used, the rotation of the active compound passes through the point of inactivity, and that by applying an arithmetical process by a purely rule-of-thumb method to numbers sometimes negative and sometimes positive, one is bound to obtain quotients also sometimes positive and sometimes negative, but this

merely indicates that the abnormality ought to be laid at the door of the substance examined.

The second of these two cases is, however, of considerable interest and will be referred to further on because it raises an interesting question in connection with normal rotation-dispersion, but before dealing with it we may revert for a moment to the case of ethyl tartrate in regard to abnormal rotation-dispersion. We have seen that at a temperature of about 80° the dispersion-rotation curve shows a maximum in the neighbourhood of the blue light, but that if the temperature be 160° there is no such maximum for these particular colours and that the same is the case if the temperature be about -40° . To say, however, as is often done, that the rotation-dispersion at the high and low temperatures is normal whereas at the intermediate temperature it is abnormal seems very arbitrary. It must be clear that if both the other two curves were extrapolated so as to include the former case, light of wave-length considerably less than violet, a maximum would be very likely to appear in the curve, whilst at the low temperature of -40° , if the rotation-dispersion curve were extrapolated, a maximum would occur, with equal probability, for light of greater wave-length than red. The term abnormal, if it is to be used at all, should be applied, not merely to the temperature-rotation curve at one temperature, but to the temperature-rotation curves for all temperatures, in fact, to the substance itself. The reason for abnormal rotation-dispersion in the light of what has already been said as regards the maximum in temperature-rotation curves seems simple. The whole curve for violet light is retarded on that for blue, that for blue is retarded on that for green, and so on, the result being that the maximum passes to a higher temperature as the wave-length of the light decreases. In the same way, since the whole curve is displaced, and since, as appears to be the case, the sweep of these curves is the same also, they intersect one another at different points, not all at one point, and this gives rise to the phenomenon of anomalous rotation-dispersion.

It may be remarked in this connection that attention has often been drawn to the fact that abnormal rotation-dispersion occurs in substances the rotation of which alters rapidly with temperature-change. The reason for this seems clear from what has just been said. It is at a distance from a maximum—roughly speaking, midway between a maximum and a minimum—that rotation changes most rapidly with alteration of temperature, and it is just in this region that the temperature-rotation curves intersect and give rise to abnormal rotation-dispersion.

The question now arises, what is normal rotation-dispersion? or, to put it otherwise, do any substances exist which differ in their behaviour from ethyl tartrate? This is a question which cannot be settled at the present time, since, although a considerable amount of material has been collected, it scarcely touches the main question because the all-important matter of temperature-change has been left out of account. Nevertheless, very many statements may be found in the literature to the effect that this substance or that has normal rotation-dispersion, and the idea seems generally to be that if the dispersion coefficient varies comparatively little, perhaps when the compound is mixed with a solvent or when its temperature is altered slightly, then the rotation dispersion is to be considered as normal. An example in which the temperature-change was very considerable is afforded by the dispersion data obtained by Pickard and Kenyon (*Trans. Chem. Soc.*, 1913, ciii., 1933). But it is, nevertheless, difficult to decide whether these substances really have normal rotation-dispersion or not. The matter may be considered in this way. It will probably be granted that the rotation of a substance for any colour of light varies at least to some extent as the temperature changes, as is the case, for instance, with the rotation of the alcohols prepared by Pickard and Kenyon. Now let us imagine that the rotation for a given substance for violet

light at a temperature t is A , and for red light is B , then the dispersion coefficient is A/B^* ; now suppose the temperature to change to t' and the rotation for violet light at this temperature to be A' , and suppose that this is less than A , that is, that the rotation diminishes as the temperature falls, let us say, from t to t' , then in order that the dispersion coefficient may be the same as before we must have $\frac{A'}{B'} = \frac{A}{B}$, B' being the rotation for the red

light at the temperature t' . Now it will be obvious that this ratio can only be preserved provided the two temperature-rotation curves for violet light and for red light are such that they intersect at the point at which the rotation for both colours of light is zero, and that beyond the temperature at which this occurs they proceed again in a similar manner, but with negative, instead of positive, rotations. From such examples as we know it is impossible to decide whether this behaviour will be, in any way, general; whether temperature-rotation curves will cut in a single point just where the rotation is zero, and it seems to the writer that the apparent normality of certain rotation-dispersions is to be ascribed to the fact these dispersion coefficients have been measured on substances the temperature-rotation curves of which happen to have a maximum value in the neighbourhood of ordinary temperatures (as is the case with Pickard and Kenyon's alcohols), and are not due, or at least not necessarily due, to any inherent peculiarity of the substances themselves. But, of course, Pickard and Kenyon's alcohols may represent a class of substances conforming exactly to the type for which the temperature-rotation curves meet exactly at zero rotation.

Nevertheless, there is one point which may be considered, for it may, after all, be essential to distinguish between two different classes of compound. We have seen already that the family of temperature rotation curves for a substance such as ethyl tartrate do not all cut in one point, and this, we have seen, was due to the fact that the maximum rotations for the different colours lie at different temperatures. Now it is quite possible that in certain other cases the maximum rotation for different colours of light may perhaps lie at the same temperature, in which case, if the sweep of the different curves were the same, the whole family of curves would cut in a single point, but of course it does not follow in any way that the rotation corresponding with the points in which they cut should be zero. No such instance as this has quite definitely been observed, but perhaps the data obtained by Pickard and Kenyon for optically active alcohols may represent a case of this sort which would account for the comparative constancy over a wide range of temperature of the dispersion coefficients, which happen to lie more or less in the neighbourhood of the maximum rotation. It is even more probable than the data already referred to, obtained by Pope and Winnill for 2-nitrotoluene-4 sulphonyl β -tetrahydroquinoline, may be of the same sort. From a study of their data for this substance, it seems very likely that if a solvent could be found in which the active compound would have a rotation of about -85° that the rotation would be identical at least for the three colours of light which they used, and perhaps it might be identical even for a wider range of colours than this.

These two classes of substances may be illustrated by two of the diagrams in the paper by Armstrong and Walker already referred to (*Proc. Roy. Soc.*, 1913, A, lxxxviii., 388). In that paper these authors have arrived at the conclusion that change of rotation, both with alteration of temperature and of solvent, is to be ascribed to a variation in the relative proportions of dynamic isomerides. Limitations of space render it impossible to point out the enormous objections which could imme-

diately be brought against any such idea. It need only be remarked here that Armstrong and Walker's diagram on p. 398 is merely another method of representing rotation-dispersion, in which the values of the rotation are plotted relative to the rotation instead of relative to wave-length, and that they do not necessarily have anything whatever to do with the presence or absence of isodynamic isomerides. Since this diagram therefore merely represents dispersion data in a new way, the deductions which can be made from it are exactly those which could be made from ordinary dispersion-rotation curves, but inasmuch as the diagram depends upon a purely arbitrary assumption, it is of course of less value. It is to be noted that the lines for the different colours drawn on their diagram intersect practically at a single point, and that the diagram differs from those on p. 397 from methyl and ethyl tartrate exactly in this respect.

These two diagrams of Armstrong and Walker represent the same thing as is shown in the diagram Fig. 7 of a paper by the present writer for ethyl tartrate (*Trans. Chem. Soc.*, 1913, ciii., 165), where there is also an intersection of temperature-rotation graphs throughout a certain range. It may possibly be that substances really exist in two classes, those for which the temperature-rotation curves or Armstrong and Walker's dispersion curves cut in a single point and those for which they cut over a range of temperature or rotation, but this is likely to be the only difference which can be discovered in regard to rotation-dispersion between various active compounds. Whether it will be wise to label one as normal and the other as abnormal remains to be seen.

Only one further matter need be referred to, namely, rotation-dispersion in solution. It has been shown by the present writer that the temperature of maximum rotation of a substance such as ethyl tartrate moves to a different temperature as the concentration is varied. Very few substances have been examined for different colours of light in various solvents and at several concentrations, but it appears very clearly from the data which have been collected by Winther for tartaric acid in water and in alcohol, that the period of intersection of the temperature-rotation curves is very similar in solution to what it is for the homogeneous substance, and further, that on dissolving the compound in a liquid this period of intersection shifts its position on a diagram in exactly the same kind of way that the maximum rotation shifts its position (see *Trans. Chem. Soc.*, 1913, ciii., 167, Fig. 9). It seems, therefore, extremely probable, in fact it seems certain, that the so-called normality of the rotation-dispersion of, say, tartaric acid in water is solely to be ascribed to the fact that the influence of the solvent is to move the maximum of the temperature-rotation curves into the ordinary temperature, and at the maximum rotation the so-called dispersion coefficient appears to be normal. This greater normality is, however, altogether imaginary, since the abnormality has merely been shifted to a different region of temperature. It is for a similar reason that the rotation-dispersion of the alkali tartrates appears to be normal.

It may perhaps be mentioned in conclusion that by the adoption of the point of view advocated in this paper and in *Trans. Chem. Soc.*, 1913, ciii., 145, a survey of all the phenomena of optical activity may be made and a comprehension of the interdependence and interrelationship of these phenomena be obtained, and in addition it may be observed that this advantage is gained independently of any theory as to the ultimate causes of the phenomena discussed. The writer's own working hypothesis as to the mechanism of these changes has been detailed in various papers, and it is perhaps only necessary to say here that the statement by Pope and Winnill (*Trans. Chem. Soc.*, 1912, ci., 2313), which is prominently quoted by Armstrong and Walker (*Proc. Roy. Soc.*, 1913, A, lxxxviii., 390), to the effect "that he has abandoned the view that internal pressure is an operative factor in connection with variations in the rotatory power," is incorrect.

* This is the ordinary way of looking at the matter. Winther's method is much better, but for reasons which cannot be entered on here it also would probably fail if applied over a wide range of temperature.

A MODIFICATION OF THE
USUAL METHOD OF CORRECTING SILICA
FOR INCLUDED SALTS.

By S. B. KUZIRIAN.

When silica, liberated by the action of hydrochloric acid upon the product of fusion of a silicate with an alkali carbonate, is made insoluble and separated by the usual subsequent treatment—viz., evaporation, desiccation at 110° , extraction with dilute hydrochloric acid and water, filtration, and repeated washing with distilled water—it invariably contains foreign material which, after strong ignition, consists essentially of oxides, free or combined with the silica. If the silica is volatilised by treatment with hydrofluoric acid and sulphuric acid, the included material is composed of sulphates which remain as such, or are changed to oxides in a subsequent ignition. If the constituents of this residue were definite and correctly determinable, it would be possible to calculate the weight of the oxides as they exist in the strongly ignited silica, and to make the proper correction; but it is a difficult task to make a correct analysis of a residue which sometimes does not exceed 2 to 3 mgrms., and may contain iron, aluminium, manganese, titanium, magnesium, sodium, potassium, &c. In order to avoid making the quantitative analysis of this small residue of sulphates and oxides, it has been an approved procedure to blast the silica to constant weight, and then to assume that after the prolonged blast ignition the impurities are left in the form of oxides. Then, after the removal of the silica with sulphuric and hydrofluoric acids, the remaining sulphate residue is also blasted to constant weight, and the assumption is made that this latter step will transform the sulphates of the residues into their oxides. The weight of silica is then found by difference. It will be shown in the following account of experimental work that the residue obtained after treatment of the blasted silica with sulphuric and hydrofluoric acids and blasting does not accurately represent the amount of included material as it is ordinarily weighed with the silica.

In the presence of moisture from the Bunsen burner or the blast lamp, chlorides are slowly decomposed with evolution of hydrochloric acid and the simultaneous formation of metallic oxides, or, in the case of the alkali metals, hydroxides, which may then enter into combination with any suitable non-metallic oxide with which they are in contact. Silica containing traces of soluble alkali chlorides may, on strong ignition, gradually combine with the metallic oxides formed, as has been shown in a previous paper (*Am. Journ. Sci.*, 1913, xxxvi., 598). The assumption that the impurity in the silica, contaminated by chlorides when it is separated, consists after the ignition exclusively of oxides is therefore well founded.

Alkali sulphates, on the other hand, do not yield definite and weighable oxides on ignition. Moreover, they may volatilise as such at the high temperature of the blast-lamp. The experiments of Table I. show that the presence of silica does not materially change this characteristic of alkali sulphates, and that when a small amount of an alkali chloride is added in solution to ignited silica, and the mixture evaporated to dryness and treated with sulphuric acid, the residue left after ignition with the Bunsen burner is essentially the neutral sulphate.

TABLE I.

Silica ignited with Bunsen burner $\frac{1}{2}$ hour.	Silica ignited with blast-lamp 20 mins.	Na_2SO_4 equivalent to NaCl added.	Increase in weight of silica after addition of NaCl treatment with H_2SO_4 and ignition with Bunsen burner.	Error when the impurity is corrected as Na_2SO_4 .
Grm.	Grm.	Grm.	Grm.	Grm.
0.4779	0.4776	0.0122	0.0131	+ 0.0009
0.5316	0.5315	0.0122	0.0131	+ 0.0009
0.5266	0.5264	0.0122	0.0122	—
0.5311	0.5293	0.0115	0.0115	—

That elements other than sodium and potassium, present originally with the silica as chlorides and converted to sulphates by the action of sulphuric acid and gentle ignition, may be recovered essentially as sulphates after treatment with sulphuric and hydrofluoric acids and gentle ignition, is shown in Table II.

TABLE II.

Silica ignited with Bunsen burner $\frac{1}{2}$ hour.	Silica ignited with blast-lamp 20 min.	Sulphate equivalent to chloride added.	Sulphate determined by increase in weight of silica.	Sulphate left after removing silica by $\text{H}_2\text{SO}_4 + \text{HF}$.
Grm.	Grm.	Grm.	Grm.	Grm.
BaCl_2 added.				
0.5290	0.5290	0.0103	0.0098	0.0104
CaCl_2 added.				
0.5576	0.5572	0.0121	0.0114	0.0118
0.5351	—	0.0242	0.0218	0.0226
0.5486	—	0.0242	0.0242	0.0234
0.5413	—	0.0242	0.0228	0.0234
0.5486	0.5486	0.0242	0.0242	—
MgCl_2 added.				
0.5441	0.5436	0.0200	0.0195	0.0197
0.5446	—	0.0200	0.0215	0.0220
0.5456	0.5456	0.0200	0.0203	—
AlCl_3 added.				
0.5456	—	0.0195	0.0200	0.0195
0.5447	—	0.0195	0.0192	0.0205
0.5490	0.5490	0.0195	0.0188	—

As is well known, sulphates other than alkali sulphates lose the acidic oxide, more or less according to the conditions, when submitted to ignition with the blast-lamp. While prolonged blast-ignition may bring about a complete transformation of the sulphates of iron, aluminium, chromium, and titanium to the respective oxides, the refractory alkali sulphates, as well as the sulphates of magnesium, calcium, and barium in large degree, will remain in the condition of sulphates (though the alkali sulphates may volatilise appreciably), and the correction for silica as ordinarily applied will be in error by an amount approximately equal to that of the sulphur trioxide combined in the sulphates.

The source of error, inherent in the usual method of applying corrections to the ignited silica, may be largely avoided by the introduction of a slight modification of the treatment. This modification consists essentially in treating the ignited silica with sulphuric acid, gently igniting again before weighing, and in igniting under exactly the same conditions the sulphate residues left after the removal of the silica in the usual way. That is to say, the included impurities of the silica must be transformed before weighing into the condition in which they will be left when the silica is removed by sulphuric acid and hydrofluoric acid. This can be accomplished by adding a few drops of dilute sulphuric acid to the well ignited impure silica, evaporating the excess of the acid slowly over a radiator, and igniting the residue by means of a Bunsen burner, before weighing the residue. Then, after the removal of the silica in the usual manner, the sulphate residue left is ignited at the same temperature and for the same duration of time as was the silica, and then weighed. From the weight of the silica plus the impurity before the treatment with sulphuric acid and hydrofluoric acids, and that of the residue after that treatment, the weight of the silica is found by difference.

Table III. contains the details of experiments in which silica was fused with six times its weight of sodium carbonate, the melt treated with hydrochloric acid, the mixture evaporated, the residue desiccated, at 110° (A), or, in presence of acetic anhydride, at 137° (B), and extracted as usual with hydrochloric acid, the precipitate filtered off

and washed, and the filtrate treated again like the original solution of the melt for the recovery of silica soluble in the former operation. The residues (first, second, and total), and the error which results from calling these residues oxide instead of sulphate and subtracting their weight from that of the ignited silica, according to the usual method of making the correction, are shown.

TABLE III.

SiO ₂ (blasted) taken.	Residue left by H ₂ SO ₄ + HF treatment of first pre- cipitate.	Residue left by H ₂ SO ₄ + HF treatment of second pre- cipitate.	Sum of residues.	Error which results from calling the residues oxide instead of sulphate.
Grm.	Grm.	Grm.	Grm.	Grm.
A.—Desiccation at 110°.				
0.5302	0.0010	0.0012	0.0022	+0.0013
0.5211	0.0010	0.0010	0.0020	+0.0012
0.5440	0.0010	0.0012	0.0022	+0.0013
0.5351	0.0010	0.0002	0.0012	+0.0007
0.5436	0.0010	0.0013	0.0023	+0.0014

B.—Desiccation at 137° in Acetic Anhydride.

0.5520	0.0010	0.0003	0.0013	+0.0008
0.5452	0.0010	0.0010	0.0020	+0.0012
0.5347	0.0010	0.0005	0.0015	+0.0009
0.5521	0.0010	0.0005	0.0015	+0.0009

These errors, which are not inappreciable, were found when the silica was separated, as well as possible, from sodium chloride alone. When chlorides of other elements, such as magnesium, calcium, and aluminium, are present, the silica separated is likely to be also contaminated with these salts, which, by the ordinary treatment, will be transformed to oxides when the silica is ignited and to sulphates when the silica is removed, and these sulphates will be more or less refractory under ignition, according to their natures and to the duration and temperature of the ignition. The errors shown above for the case in which sodium chloride is the only contaminating salt are likely to be magnified in the analysis of ordinary silicates of complex composition. The proposed modification of treatment will therefore lead to a more accurate application of the correction for impurities included in the silica. In this procedure it is not necessary to blast either the silica or the residue before and after the removal of silica as silicon fluoride. The Bunsen burner will give a temperature sufficiently high to volatilise the excess of sulphuric acid, and to break up the acidic and pyrosulphates of the alkali elements. The included salts being weighed as sulphates, or as sulphates broken up to practically the same extent in both ignitions, the correction to be applied will be reasonably accurate.—*American Journal of Science*, xxxvii., p. 61.

A NOTE ON THE PREPARATION OF TELLURIC ACID AND A TEST FOR ASSOCIATED TELLUROUS ACID.

By PHILIP E. BROWNING and H. D. MINNIG.

OF the various methods suggested for the preparation of telluric acid, two only seem to be in general use:—First, the oxidation of tellurous acid by chromic acid (Staudenmaier, *Zeit. Anorg. Chem.*, x., 189; Gutbier, xxix., 22), and the precipitation of the telluric acid by nitric acid after the concentration of the solution; and second, the oxidation of an alkali tellurite by hydrogen dioxide, followed by the precipitation of the telluric acid by nitric acid (Gutbier, *Zeit. Anorg. Chem.*, xl., 260). While both of these methods give quite satisfactory yields, the difficulty of washing out the chromium salt in the first method (Kothner, *Annalen*, cccix., 39), and of removing the alkali salt in the second method is apparent. Berzelius formed tellurates by passing chlorine into an alkaline solution of a

tellurite, but here also the precipitation of the telluric acid would have the same disadvantage in the inclusion of alkali salts.

The work to be described was undertaken to study the effect of free chlorine upon elementary tellurium suspended in water. The element in the form of an amorphous powder weighing several grms. was suspended in water and subjected to the action of a current of washed chlorine gas. After about an hour the tellurium had dissolved, and a portion of the solution, made alkaline and then acidified with acetic acid, remained clear, showing the complete oxidation to telluric acid.

It was found by experimentation with solutions of tellurates and tellurites that this method of testing would detect a mgrm. of tellurous acid in the presence of between 100 and 200 mgrms. of telluric acid, in a volume of 5 cc.

When the solution was thoroughly saturated with chlorine and the complete oxidation was shown by this method of testing, the solution was evaporated to small volume, tested to be sure that no reduction had taken place, and again treated with chlorine if necessary. The concentrated solution was then treated with acetone or ethyl alcohol to the complete precipitation of a beautifully crystalline product of satisfactory yield. This product was washed with acetone or alcohol until the washings gave no test with silver nitrate for hydrochloric acid.

The telluric acid obtained was readily soluble in water; moreover, the solution gave no indication of the presence of tellurous acid on treatment with an alkali hydroxide and acetic acid, and was not reduced by stannous chloride except on warming.

After concentration of the telluric acid solution, the acid may be precipitated by nitric acid, washed with the same reagent to remove the hydrochloric acid, and then with acetone or ether to remove the nitric acid. This modification of the process, however, appeared to have no advantage in the purity of the product.

The absence of contaminating salts is practically assured by the method described if the elementary tellurium used is reasonably pure.—*American Journal of Science*, xxxvii., p. 72.

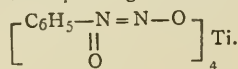
THE USE OF THE AMMONIUM SALT OF NITROSOPHENYLHYDROXYLAMINE
"CUPFERRON"
IN THE QUANTITATIVE SEPARATION OF TITANIUM FROM IRON.*

By WILLIAM M. THORNTON, JUN.

NITROSOPHENYLHYDROXYLAMINE was first synthesised by Wohl (*Ber.*, 1894, xxvii., 1435). The ammonium salt of nitrosophenylhydroxylamine was brought into service in analytical chemistry by Baudisch (*Chem. Zeit.*, 1909, xxxiii., 1298) for the estimation of either copper or iron, the separation of these two metals from various others, and indirectly for the separation of the former from the latter. Owing to these properties the trivial name of "cupferron" has been applied to the ammonium salt of nitrosophenylhydroxylamine. The analytical data given by Baudisch are few and not absolutely confirmatory. Since then, however, various other workers (notably Biltz and Hödtke, *Zeit. Anorg. Chem.*, 1910, lxvii., 426; Hanus and Soukup, *Ibid.*, 1910, lxviii., 52; and Fresenius, *Zeit. Anal. Chem.*, 1911, l., 35) have thoroughly demonstrated the value of this reagent for the quantitative precipitation of either copper or iron and their separation from various other bodies. In connection with other work, Schroeder (*Zeit. Anorg. Chem.*, 1911, lxxii., 89) has made the statement (*loc. cit.* p. 95) that titanium and zirconium could be quantitatively precipitated from their acid solutions by the "cupferron" reagent, and that experiments were in progress for the

* From the *American Journal of Science*, vol. xxxvii., p. 173.

estimation of these two elements. Schroeder, however, gave no experimental data, and has not published further upon the subject. Bellucci and Grassi (*Gazzetta Chimica Italiana*, 1913, Anno xliii., parte I., 570) have shown that from solutions, moderately acidified with either sulphuric or hydrochloric acid, titanium could be quantitatively precipitated by the "cupferron" reagent, and that titanium could also, under these conditions, be quantitatively separated from aluminium. Under these circumstances the titanium comes down as a very bulky, readily filterable, precipitate of canary yellow colour. In the opinion of the aforesaid authors the precipitate, after having been crystallised from ethyl alcohol, is the titanic salt of nitrosophenylhydroxylamine, corresponding to the formula—



It has been known for a long time that certain organic acids, containing both hydroxyl and carboxyl groups, such as tartaric acid and citric acid, have the power to prevent the precipitation of certain metals when their solutions are made alkaline with sodium or potassium or ammonium hydroxide. This principle was made use of by Gooch (*Proc. Am. Acad. Arts and Sci.*, n. s., vol. xii., p. 435; *CHEM. NEWS*, lii., 55, 68) for the separation of titanium from iron; for, if the solution contain sufficient tartaric acid, the iron can be precipitated by ammonium sulphide as ferrous sulphide, and the titanium will then be found entirely in the iron free filtrate. The next step is to oxidise the tartaric acid; for titanium is not precipitated in its presence by any of the reagents previously used for its gravimetric estimation. This was accomplished by Gooch (*loc. cit.*, p. 445), after strongly acidifying with sulphuric acid by adding potassium permanganate to the boiling aqueous solution. This process is open to the objection that a great deal of manganese is thus introduced into the solution and is co-precipitated in some measure when the titanium is subsequently thrown down by hydrolysis of titanic acetate. A second precipitation is therefore necessary, which must be preceded by fusion with an appropriate flux and solution of the melt in acid. The author's experiments show that, after acidifying the filtrate from the ferrous sulphide, the titanium can be quantitatively precipitated by the "cupferron" reagent, notwithstanding the presence of tartaric acid.

Two solutions of titanic sulphate were employed for these experiments; which were prepared by warming potassium fluotitanate with concentrated sulphuric acid until all the hydrofluoric acid had been volatilised, pouring into cold water, and making up to known volume. The quantity of sulphuric acid used was such that the resulting solution contained about 10 per cent of absolute acid. In the case of the second solution, the trace of platinum was removed by saturating the solution with hydrogen sulphide, filtering off the platinic sulphide, boiling out the hydrogen sulphide, filtering again, and making up the solution to definite volume. The first solution was standardised by taking weighed portions of 25 cc. and precipitating the titanium by hydrolysis of the acetate. The solution was made nearly neutral with re-distilled ammonium hydroxide—until a faint permanent turbidity appeared. One cc. of a strong solution of ammonium hydrogen sulphide was added, followed by 15 grms. of ammonium acetate and 20 grms. of glacial acetic acid, and the solution made up to 400 cc. This solution was brought rapidly to boiling and maintained in ebullition for one minute. The precipitate was washed twenty times—first with boiling 5 per cent acetic acid, and finally with boiling water. In the usual manner the precipitate was ignited to titanic oxide and brought to constant weight over the Meker burner. Duplicate determinations gave the following results:—

Titanic sulphate solution.		Titanic oxide.	
(a) 25 cc. = 37.308 grms.	0.1427 grm.	0.5226 per cent	
(b) 25 cc. = 27.319 grms.	0.1428 grm.	0.5227 per cent	

Since these two values agreed so closely, (b) was arbitrarily taken as correct. The second solution was standardised by taking two weighed portions of 25 cc. and 24 cc. respectively and determining the titanium in one (a) by the acetate method given above, and in the other (b) by "cupferron" method of Bellucci and Grassi (*loc. cit.*) (the exact technique of which will be given presently). Duplicate determinations gave the following results:—

Titanic sulphate solution.		Titanic oxide.	
(a) 25 cc. = 27.814 grms.	0.1066 grm.	0.3832 per cent	
(b) 24 cc. = 26.667 grms.	0.1022 grm.	0.3832 per cent	

Since these two determinations agreed exactly, the value here obtained was taken as correct.

A solution of ferric sulphate was prepared by dissolving Baker's analysed ferric ammonium sulphate in water, adding 25 cc. of concentrated sulphuric acid per litre to prevent the formation of basic salt, filtering, and making up to definite volume. In one portion (a) of 25 cc. the iron was determined by titration with potassium permanganate after reduction by zinc—the potassium permanganate having been previously standardised against sodium oxalate. (The sodium oxalate was obtained from the Bureau of Standards, Washington). In another portion (b) of 25 cc. the iron was determined by precipitation with re-distilled ammonium hydroxide in a platinum basin and ignition of the precipitate to ferric oxide. Parallel determination gave the following results:—

Ferric sulphate solution.		Titanic oxide.	
(a) 25 cc.	0.2267		
(b) 25 cc.	0.2269		

The value obtained in (a) by the volumetric method was arbitrarily taken as correct.

The supply of "cupferron" for these experiments was prepared in this laboratory according to the directions given by Baudisch (*Chem. Zeit.*, 1911, xxxv., 913). An approximately 6 per cent solution of the salt was made by dissolving it in cold water and filtering from any insoluble residue that remained.

The first series of experiments was carried out with a view to ascertaining whether or not titanium could be completely precipitated and accurately determined in the presence of tartaric acid. To a solution containing a known quantity of titanium a little more than three times the weight of the titanic oxide present was added of tartaric acid. The solution was made neutral to litmus with ammonium hydroxide, then acid again with 5 cc. of sulphuric acid (made by diluting acid of sp. gr. = 1.84 with an equal volume of water), and the volume made up to 200 cc. A little more than the calculated amount of "cupferron" solution was added, and the beaker set aside for the precipitate to settle. The supernatant liquid was tested by adding a few drops of the reagent, which were made to run down the wall of the beaker. The formation of a white precipitate of nitrosophenylhydroxylamine indicates that the reagent has been added in excess, while the formation of a yellow turbidity shows that the titanium had not been completely thrown out. It is well also to test the filtrate. The precipitate was filtered on paper, using very gentle suction, and washed twenty times with cold water. During the washing the suction should be almost stopped to prevent the wash water from running through too fast to accomplish much solvent work. The precipitate is very prone to develop mud cracks, and should therefore be agitated with the stream of water from the wash-bottle as much as possible. After having been sucked free from drainage water, the precipitate along with the filter was placed in a tared platinum crucible, dried at 110° C., very carefully heated until the volatile products of destructive distillation had escaped, the inclined open crucible ignited till all carbon had been consumed, and finally brought to constant weight over the Meker burner. If it is desired to save time, the precipitate can be dried by inclining the crucible, supporting the lid tongue downward on the triangle and edge of the crucible, and applying a

small flame beneath the lid. The heat is thus deflected downward, and the precipitate gradually dried from above with little danger of spattering (see Treadwell, "Analytical Chemistry," 1910, translated by Hall, vol. ii., p. 29). It is inadvisable to dry the precipitate in the funnel; for at a low temperature the substance melts, or at least assumes a plastic condition, and penetrates the pores of the filter; moreover, the dried material is very brittle, and on attempting to fold the paper and introduce it into the crucible particles are likely to fly away and be lost. In experiments (1) and (4) the filtration was carried out on asbestos in the perforated platinum crucible. Due to the above mentioned property, a little titanous oxide was found on the outer surface of the crucible after ignition. This method of filtration was therefore abandoned. Table I. contains the results of three experiments:—

TABLE I.

No.	TiO ₂ taken, Grm.	TiO ₂ found, Grm.	Error, Grm.	Tartaric acid, Grm.
1.	0.1428	0.1426	-0.0002	—
2.	0.1428	0.1429	+0.0001	0.5
3.	0.1066	0.1063	-0.0003	0.4

In the second series of experiments actual separation of titanium from iron was carried out. To facilitate the reduction of the iron the solution, to which tartaric acid equal to three times the weight of the titanous oxide and ferric oxide present had been added, was neutralised by ammonium hydroxide, 1 to 2 cc. of sulphuric acid (1 : 1) added, and the volume made up to about 100 cc. Hydrogen sulphide was then introduced till the solution appeared colourless. If the iron is not thus reduced before its precipitation, titanium will be thrown down in part also (A. Cathrein, *Zeit. Kryst.*, 1882, vi., 243; 1883, vii., 250). The solution was then made ammoniacal and more hydrogen sulphide introduced until the iron had been completely precipitated as ferrous sulphide—leaving the solution, however, alkaline to test-paper. The ferrous sulphide was filtered off and washed ten times with very dilute colourless ammonium sulphide. The filtrate was acidified with 25 cc. of sulphuric acid (1 : 1), the hydrogen sulphide boiled out, the acid partially neutralised with ammonium hydroxide so as to leave about 2.5 cc. of sulphuric acid (1 : 1) for every 100 cc. of the solution, and the "cupferron" added in the cold. Table II. contains the results of four experiments.

TABLE II.

No.	TiO ₂ taken, Grm.	Fe ₂ O ₃ taken, Grm.	TiO ₂ found, Grm.	Error, Grm.
4.	0.1428	0.2267	0.1424	-0.0004
5.	0.1428	0.2267	0.1430	+0.0002
6.	0.1066	0.2267	0.1068	+0.0002
7.	0.1063	0.2267	0.1061	-0.0002

In the third series of experiments the solution containing the titanium and iron was divided into two aliquot parts by weight. In one part the titanium was determined by the method already outlined. In the other part the iron was determined by the method of Gooch and Newton (*Am. Journ. Sci.*, 1907, xxiii., 365). Table III. contains the results of two experiments.

TABLE III.

No.	TiO ₂ taken, Grm.	Fe ₂ O ₃ taken, Grm.	TiO ₂ found, Grm.	Fe ₂ O ₃ found, Grm.	Error TiO ₂ , Grm.	Error, Fe ₂ O ₃ , Grm.
8.	0.0716	0.1130	0.0719	0.1130	+0.0003	0.0000
9.	0.0717	0.1129	0.0716	0.1135	-1.0001	+0.0006

From the work of Bellucci and Grassi (*loc. cit.*), Fresenius (*loc. cit.*), and the author, it would seem that there should be no great difficulty attending the separation of titanium from iron, aluminium, and phosphoric acid, which are the substances with which titanium is commonly associated in nature. Experiments are now in progress by the writer for accomplishing this separation with the aid of the "cupferron" reagent, and the results will appear later.

ON THE PREPARATION OF TELLUROUS ACID AND COPPER AMMONIUM TELLURITE.

By G. O. OBERHELMAN and P. E. BROWNING.

OCCASION having arisen to prepare some tellurous acid from residues from the electrolytic refining of copper (furnished through the kindness of the Baltimore Copper Co.), residues containing a high percentage of tellurous oxide together with small amounts of silica, copper, selenium, and several other impurities, it was determined to try the effect of the solvent action of ammonium hydroxide, followed by the precipitation of the tellurous acid from the ammoniacal solution by acetic acid. This procedure, employed on another occasion for the removal of selenium (Browning and Flint, *Am. Journ. Sci.*, 1909, [4], xxviii., 112), proved satisfactory for the removal of the greater part of the silica and of those bases which are insoluble in ammonium hydroxide. By dissolving the tellurous acid thus obtained in sodium hydroxide and precipitating the tellurous acid again by acetic acid, copper and many other metals whose hydroxides are insoluble in sodium hydroxide were also removed.

If the precipitation of the tellurous acid by acetic acid is brought about without warming the solution, and the product is dried without heating, the tellurous acid obtained is readily soluble in the alkali hydroxides. If, however, the precipitation takes place in hot solution and the precipitate is dried by application of heat, the product tends to be quite insoluble in the alkali hydroxides.

After the first treatment of the residues with ammonia in this extraction process, it was observed that a purple crystalline salt separated from the alkaline solution on standing. The colour suggested a copper compound, and after the removal of this salt by filtration, the filtrate proved to be practically free from copper. It was found that a salt similar in appearance could be produced by allowing an ammoniacal solution of tellurous acid containing some copper salt to evaporate over sulphuric acid and in the presence of soda-lime. The depth of colour varied with the concentration of the copper solution from a reddish purple through pink to nearly white. It was found that a salt which appeared to be identical with the compound just mentioned could be produced by adding slowly, with constant stirring, acetic acid to an ammoniacal solution of tellurous oxide and copper chloride. The precipitate thus obtained proved to be slightly soluble in water but insoluble in acetic acid and in 50 per cent alcohol. A sample of this compound prepared in the manner just described, which from its intensity of colour was considered to contain the maximum amount of copper, gave the following analysis:—

TeO ₂	..	..	..	..	..	83.84
CuO	..	..	..	..	..	4.63
NH ₃	..	..	..	..	..	5.22
H ₂ O	..	..	..	..	..	6.10

99.79

The TeO₂ was determined by the permanganate method. Copper was estimated colorimetrically by comparing in Nessler tubes ammoniacal copper solutions of known strength with weighed amounts of the compound dissolved in acid and made ammoniacal. This method was found to be accurate to 2/10ths of a mgrm. The ammonia was determined by distillation from an alkaline solution into standard acid. The water could not be determined by difference on ignition owing to a slight reduction of the tellurium. So the compound was heated at 140°, and the residual ammonia was determined after weighing. From the weights of the total ammonia and of the residual ammonia at 140°, together with the total loss on heating at 140°, the weight of the water was determined. The loss of ammonia which resulted from heating at 140° proved to be about constant and amounted to a third of the total

ammonia. The colour of the substance changed on heating at 140° from reddish purple to blue.

It was thought that compounds of a similar nature containing bases other than copper might be formed in a similar manner. Nickel, cobalt, zinc, cadmium, and silver were tried, but with no success. Silver gave a yellow precipitate, but this proved to be the ordinary silver tellurite.

—*American Journal of Science*, xxxvi., p. 299.

ERRORS IN GAS ANALYSIS DUE TO ASSUMING THAT THE MOLECULAR VOLUMES OF ALL GASES ARE ALIKE.*

By GEORGE A. BURRELL and FRANK M. SEIBERT.

Introduction.

THE Bureau of Mines in the course of various investigations has sampled and analysed the gases found in coal and metal mines, those that flow from wells in oil and gas fields, and those produced during the processes of combustion in furnaces. In determining the purity of certain combustible gases by the method of slow combustion, the authors found that in some analyses the volume of carbon dioxide and the contraction produced by the combustion did not agree with the theoretical value, according to the equations ordinarily used for showing the reaction. Also, in analysing some natural gases by the same method the paraffin hydrocarbons present totalled over 100 per cent. The differences were greatest when the oxygen taken was only a few cc. in excess of that required to burn the gas completely. The variations could not be attributed to experimental errors, because all the analyses were carefully performed in duplicate, and the gas burettes were accurately calibrated. Consequently, an inquiry was made to determine the errors that might arise in the combustion method of analysis, by assuming that the molecular volume (the quotient of the molecular weight divided by the density) is the same for every gas. This paper presents the results of that inquiry, and is published by the Bureau of Mines because these results show the need of applying corrections in some exact analyses of certain gases by the combustion method.

In working out the results, the authors wish to acknowledge the valuable assistance of G. A. Hulett, chief chemist of the bureau.

Deductions of Wohl and Haber.

Wohl has shown that the errors due to the assumption stated are considerable ("Calculation of Gas Analysis by Combustion," *Ber.*, 1904, xxxvii., 429), but the authors of this paper are not entirely in accord with some of his deductions. Wohl derives expressions for the molecular volumes from determinations taken from a table given by Nernst ("Theoretical Chemistry, 2nd Edition, 1898, p. 44). These values agree closely with the latest determinations except in the case of methane. The value for methane is given as 1.002 at 0° C. and 760 mm. Baumé and Perrot found it to be 0.999, as shown in the table of specific gravities (Table III., *prox.*).

Wohl's gas-analysis apparatus differs from the one used in the work herein reported in that his measurements were made at constant volume instead of constant pressure. Wohl made the mistake of assuming that the expressions he derived as showing the exact proportions of certain gases entering into reaction with each other could be used in all cases. The fact is that his equations apply only when the carbon dioxide produced by the combustion constitutes between 95 and 100 per cent of the total quantity of gases remaining after combustion. It is true, as he stated, that in the case of hydrogen, carbon monoxide, and methane the quotient of the molecular weight divided

by the density at 0° C. and 760 mm. (the molecular volume) approximates very closely the value 22.412 for an ideal gas, but in the case of carbon dioxide the value becomes 22.268. He therefore concludes that Avogadro's theory does not hold in this case.

Haber ("Thermodynamics of Technical Gas Reactions," 1906, p. 306) does not consider Wohl's conclusions valid. He demonstrates his objections as follows:—

From Van der Waals's equation, the ratio between the pressure P , the volume V , and the temperature T of a gas is expressed thus:—

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT.$$

Further, if d = density at 0° C. and 760 mm. pressure, and M the molecular weight, the following equation is derived:—

$$\frac{M}{d} = (1 + a)(1 - b) = R.$$

For carbon dioxide Van der Waals gives the following values:—

$$a = 0.00874 \quad b = 0.00230$$

Therefore—

$$\left(\frac{M}{d}\right) 1.00646 = R = 22.412.$$

The value $\frac{M}{d} = 22.268$ = volume of a gram. molecule, then—

$$\frac{22.268}{22.412} = \frac{\text{molecular volume of carbon dioxide}}{\text{molecular volume of oxygen}}.$$

This value is the same as that obtained by dividing the theoretical specific gravity by the observed specific gravity.

Haber therefore concludes that the deviation in the case of carbon dioxide is due only to the fact that at 0° C. and 760 mm. pressure carbon dioxide is not a perfect gas, and that the deviation has nothing to do with Avogadro's theory. Haber further shows from Van der Waals's equation that when V is large the term $\frac{a}{V^2}$ is negligible, and that the difference between V and $(V - b)$ is also negligibly small. The equation then becomes—

$$PV = RT = C.$$

Hence, as the partial pressure of a gas decreases from one atmosphere, the gas will more nearly behave like an ideal gas, or, in other words, there can be obtained some partial pressure at and below which the behaviour of the gas will differ so slightly from that of an ideal gas that the deviation will be negligible in eudiometry. This partial pressure can be obtained by diluting the gas whose behaviour deviates from that of an ideal gas with one, or a mixture of two or more gases, whose behaviour at 0° and 760 mm. pressure is sufficiently close to that of a perfect gas. Air, the chief constituents of which are oxygen and nitrogen, can be used.

In view of these facts Haber concludes that in order to avoid the use of corrected equations in calculating the percentages of combustible gases from the combustion data afforded by a gas analysis, such a small quantity of the combustible gas should be taken for the analysis that the carbon dioxide produced by the combustion does not exceed 30 per cent of the total quantity of gas measured; that is, its partial pressure should not exceed 30 per cent of the total pressure after combustion.

Authors' Comments on Work of Wohl and Haber.

In summing up the work of Wohl and Haber regarding the true molecular volume of gases the authors of this paper comment as follows:—

1. In exact gas analysis by slow combustion, Wohl's observation that the combustion data must be corrected when the partial pressure of the carbon dioxide produced is high has been confirmed.

* *Technical Paper* 54, Department of the Interior, U.S.A. Bureau of Mines.

2. The authors agree with Haber that Wohl's expressions can be used only in special cases when the partial pressure of the carbon dioxide constitutes nearly 100 per cent of the total pressure.

3. The authors disagree with Haber's conclusion that the best method of making combustion analyses is to keep the partial pressure of the carbon dioxide so low (less than 30 per cent of the total pressure) in the gases measured after the combustion as to eliminate the use of corrected equations. Their conclusion is reached by reasoning as follows:—

Sources of Error in Gas Analyses.

In the analyses of some mixtures rich in combustible gases so small a proportion of the original gas has to be used in order to keep the partial pressure of the CO_2 produced below 30 per cent that a small error of manipulation is magnified many times when the calculation to a percentage basis is made. In many forms of gas analysis apparatus such errors are unavoidable, and even in the use of apparatus designed for exact work they occur to some extent.

The point is illustrated by the following data relating to an analysis of natural gas by the explosion method (Table I.). For the analysis only a small proportion of the sample was taken.

TABLE I.—Analysis of a Sample of Natural Gas by the Explosion Method.

	Cc.
Volume of sample taken	7.0
Volume after carbon dioxide absorption	7.0
Air added	93.0
Total volume	100.0
Volume after explosion	85.5
Contraction	14.5
Volume after absorption of carbon dioxide ..	77.3
Carbon dioxide produced	8.2

If x = partial methane
and y = partial ethane,
then $2x + 2.5y = 14.5$,

$$x + 2y = 8.2,$$

From which $x = 5.68$,

$$y = 1.26,$$

$$\text{CH}_4 = 81.1 \text{ per cent,}$$

$$\text{C}_2\text{H}_6 = 18.0 \text{ per cent.}$$

Total paraffins = 99.1 per cent.

If one makes an error of, say, $+0.1$ cc. in reading the volume after explosion and an error of -0.1 cc. in reading the carbon dioxide absorption, the figures become:—

$$2x + 2.5y = 14.4$$

$$x + 2.0y = 8.4$$

$$x = 5.2$$

$$y = 1.6$$

$$\text{Percentage of CH}_4 = 74.3$$

$$\text{Percentage of C}_2\text{H}_6 = 22.8$$

Percentage of total paraffins = 97.10, or a difference of 2 per cent

The results of an analysis of a sample of methane by the explosion method are also illustrative (Table II.).

TABLE II.—Analysis of a Sample of Pure Methane.

	Cc.
Volume of sample taken	8.0
Volume after carbon dioxide absorption	8.0
Air added	92.0
Total volume	100.0
Volume after explosion	84.0
Contraction	16.0
Volume after absorption of carbon dioxide ..	76.0
Carbon dioxide produced	8.0

If an error of ± 0.1 cc. be made in reading the volume after the carbon dioxide absorption, then hydrogen,

carbon monoxide, or some hydrocarbon other than methane is indicated. If instead of the carbon dioxide reading being 8, it was 7.9, then instead of the methane calculating to 100 per cent, it would calculate to only 98.7 per cent—a difference of 1.3 per cent. Therefore if one were examining a gas for its purity one could not be sure whether or not there was some other gas present, at least to the extent of 1 per cent.

In many cases, however, the partial pressure of the carbon dioxide can be kept low, the use of corrected equations being thus avoided. At the same time such a quantity of the sample can be used for analysis as not to increase the experimental error appreciably. For instance, the partial pressure of the carbon dioxide can be kept low in mixtures containing small proportions of methane, carbon monoxide, ethane, coal-gas, blast-furnace gas, or producer gas. But for mixtures in which the carbon gases constitute almost the whole of the sample it is much better to use the slow combustion method, taking such a quantity of the sample that the oxygen added for combustion will be only a few cc. in excess of that theoretically required, and applying corrected equations.

(To be continued).

THE SCIENTIFIC WEE .

(From Our Own Paris Correspondent).

THE SOLAR STORMS.

The magnetic storms of the sun that cause the magnet needle to vibrate at a distance of more than 150,000 kilometres, and which disturb the telephonic communication of our planet, are, as we are aware, particular phenomena of the solar activity. These storms take place in the spots of the sun, which spots are regulated by a general law, the cause of which is not yet discovered, but which makes them increase and decrease periodically, following a rhythm of about eleven years. The origin of these spots remains, however, still mysterious. Very recent researches by Dr. J. A. Harker, of the National Physical Laboratory, will very probably somewhat elucidate these obscure phenomena. This learned man has studied the electrical emissivity of matter, and he has noticed that this said emissivity is intimately related to the problem of incandescent lighting. Mr. Harker recalls to mind the fact that the conductivity of bodies is only a question of temperature. At very high temperatures all bodies are conductors, and this is so true that in those conditions no good isolators are known. Some years ago Guthrie had observed that an iron sphere charged with electricity loses its charge at a red-heat, if it is electrified positively, and also at a white-heat whatever may be the nature of its electricity. The phenomenon of emissivity of matter was studied for the first time by Elster and Geitel, then by Richardson. All these *savants* have remarked that metals and carbon at high temperatures emit electrified particles. At somewhat lower temperatures, during the expulsion of the impurities and the gases of the metals, the particles are positive. At very high temperatures these particles are negative. But the emission of particles negatively electrified is much more considerable than the emission of positive particles. This law seems to be general. All heated metals emit electricity in the form of currents. Very recent observations of two American astronomers, Messrs. Hale and King, of the Mount Wilson Observatory, have shown that powerful magnetic fields exist in the sun; this seems necessary for the explanation of certain phenomena of the sun's spots, as the result of the emission of swarms of electrical charged particles. The formidable magnetic whirlwinds, the powerful electrical discharges which take place in the sun, and which give birth to the Hertzian waves, and the cathodic rays emitted by the sun, have no other cause than the fusion of the metals in the solar furnace.

THE VARRON OF THE OX.

A new and important communication has just been made to the Academy of Sciences by M. Edmond Perrier, Director of the Natural History Museum, in the name of M. Adrien Lucet, Member of the Academy of Medicine, concerning the hypoderm fly or *varron* of the ox. The larvæ of these flies secrete under the skin of the back of the ox, where they increase in size and cause abscesses. The animals attacked in this way grow thin and the flesh is unserviceable, and their hides become pierced like a sieve. For these reasons agriculture and the leather industry lose enormous sums annually. In order to extract the larvæ the only means known up till now was to press the abscesses enclosing them with the hands, or else, after having opened the tumour, to take them out with the help of pincers. According to numerous experiments he has performed, M. Lucet affirms that it is possible to destroy this parasite in the bovine species in the subdermic tumours where they live by the aid of the injection into these tumours of a few drops of tincture of iodine.

THE MINERVITES.

The minervites are double phosphates of alumina and alkali that M. Armand Gautier discovered in 1892 in the grottoes of Minerva in the Herault Department. Since then they have been met with in diverse places, in the Island of the Reunion, in the province of Oran, &c., but always in grottoes where primitively had become accumulated animal deposits and excrements, transformed first into guano, then into alkaline phosphates that have attacked the aluminous outer rock. These minervites are white substances, or else slightly tinted with yellow resembling kaolin, but containing 40 per cent of phosphoric acid and as much as 15 and 16 per cent of potash. It is easy to understand what a treasure and richness they would represent for agriculture if continuous banks of minervites were discovered. In the grotto of Minerva they are found in contact with the Permian red sandstone rocks in stratifications discordant with the nummulitic. They there fill kinds of pockets to which is superposed a thick layer of earthy and clayey phosphates, amongst which are scattered very large quantities of the bones of the cave bears, of rhinoceros, of hyænas, of small gnawing animals, of bats, &c. The deposit discovered in 1892 by M. Armand Gautier represents not less than 100,000 tons of phosphated manure.

AN ELEGANT METHOD FOR DETERMINING THE DIFFERENCES OF LONGITUDE.

Prof. Lippmann has just discovered an exceedingly ingenious photographic method which enables the measuring of the difference of longitude existing between two localities. This method consists in taking simultaneously at each of the two stations a photograph of the sky, placing at the zenith an artificial star. By reducing these two photographs in the same way as is done for the photographic map of the sky, it is easy to calculate the difference of longitude to about a fraction of a second of an arc or segment, that is to say, with an uncertainty of merely scarcely 3 or 4 metres.

THE ROLE OF LICE AND THEIR DESCENDANTS IN THE TRANSMISSION OF INFECTIOUS DISEASES.

Dr. Roux, of the Pasteur Institute, has presented to the Academy of Sciences a paper of MM. Sergent, Folley, and Viola on the experimental transmission to men and monkeys by the intermediary of the louse, not only of intermittent fever, but of exanthematic typhus and probably of various other affections. The microbe of typhus is hereditary in the descendants of the louse; that is to say, that the egg, the larva, and the parasite itself are infected from generation to generation. This is the first time that this has been remarked, and naturally it vastly increases horror of these detestable little insects.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, April 2, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

THE Bakerian Lecture was delivered by Prof A. FOWLER, F.R.S.

Series Lines in Spark Spectra.

This investigation was undertaken in continuation of that on the new lines (λ 4686, &c.) produced in 1912 by passing strong discharges through helium tubes containing an impurity of hydrogen. These lines are of great interest in celestial spectroscopy, and, following Rydberg, they were at first attributed to hydrogen. They have since become of increased importance, in connection with theories of the constitution of the atom, through the theoretical work of Dr. Bohr, who explains them as being produced during the first stages in the reformation of helium atoms from which both electrons have been removed by the strong discharges employed.

Certain peculiarities of the "4686" series suggested a search for other series of similar character, in order that some generalisation with regard to them might be reached. Further experiments on magnesium have yielded many new enhanced (spark) lines, and valuable data for calcium, strontium, and barium have been provided by the work of other observers. The chief results may be summarised as follows:—

1. Enhanced (spark) lines form series which occur in groups similar to those previously recognised in arc spectra. The formulæ representing enhanced lines, however, differ from those employed for arc lines in that Rydberg's constant "N" (= 109,675 for Rowland's scale) has a value equal to 4N.
2. The fundamental series, in the case of enhanced lines, derives its limit, and the separation of its components, from an observed negative term of the diffuse series. The well known spark line of magnesium, λ 4481, is the first member of such a fundamental series in association with a newly-discovered system of doublets.
3. No numerical relations have been traced between any of the enhanced line series and the series of arc lines of the same elements.
4. The "4686" series produced in helium tubes is of the enhanced line (4N) type, and can no longer be considered to belong to the same group as the Balmer series of hydrogen lines, which is of the arc (N) type. The "4686" series and the associated "Pickering" lines, as indicated by Bohr, are in all probability due to helium, and should be designated "proto helium" lines in accordance with the nomenclature of Lockyer.
5. Analogy with the "4481" series of magnesium suggests that the "4686" series of proto-helium is primarily of the fundamental type, while the three associated series may be considered to be coincident with it. The Pickering lines are represented in magnesium by a combination series which is derived from the fundamental.
6. Bohr's theoretical formulæ for hydrogen and helium are in close accordance with the facts of observation. Adopting these formulæ, the spectroscopic data at present available give the mass of the hydrogen atom in terms of the mass of the electron as 1836 ± 12 .

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, April 1, 1914.

Mr. A. CHASTON CHAPMAN, President, in the Chair.

MESSRS. Robert Bickerstaffe, Thomas Henry Byrom, Sydney George Clifford, Donald Richard Frazer, and John McLaren were elected Members of the Society.

Certificates were read for the second time in favour of Messrs. Lauchlan Henry Dyke Acland, Frederic Herbert Lees, William Henry Woodcock, and Walter Alan Gibbings.

The following papers were read :—

"*The Water of Dorton Spa.*" By C. AINSWORTH MITCHELL.

Dorton: A forgotten Spa. Brief outline of history. A remarkable water. Iron (46 parts per 100,000) present as basic sulphate. Analyses by Prof. Brand (circ. 1830). Present composition of the water.

"*On Damage caused to Vegetation by Sulphurous and Sulphuric Acid in the Atmosphere.*" By R. R. TATLOCK and R. T. THOMSON.

The mere fact of the presence of sulphates in plants in excess of the proportion found in vegetation grown in a pure atmosphere is no proof of damage by sulphur acids.

This is shown by results of analysis of plants from various localities, and the authors conclude that such damage can only be proved if (1) the percentage of SO_3 is considerably above that present in the plant normally, and (2) the leaf or other part of the plant, when moistened on the surface with water, gives an acid reaction with litmus, phenolphthalein not being admissible.

"*The Abnormal Refraction of Milk Serum.*" By J. McCRAE.

The author gives some results he has obtained during the analysis of certain abnormal but genuine milks produced in the Transvaal. The milk serum obtained from the samples, when examined by the Zeiss Immersion Refractometers at 20°C . gave results as low as 32.3. The normal minimum refraction of milk serum has been previously shown by the author to be 36 when, as in the present cases, the reagent employed for coagulation is sulphate of copper.

The cattle were apparently in good condition and the veldt grass was plentiful.

NOTICES OF BOOKS.

Photo-Chemistry. By S. E. SHEPPARD, D.Sc. (Lond.). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

THE establishment of photo-chemistry as an independent branch of science may now be regarded as definitely accomplished, and this text-book will probably be for some time used as a standard work on the subject. It has many merits, prominent among them being its completeness and the fullness of its bibliographical references. The measurement of light quantities is first discussed, with short descriptions of the apparatus employed for the purpose, and the classification of light sources according to their economic and energetic relations is well treated. The statics and dynamics of photo-chemical change and the consideration of light as the resultant of chemical change are subjects which are discussed in great detail, and a chapter is devoted to organic photosynthesis, with special reference to the building up of food stuffs by chlorophyll. It is occasionally not easy to arrive at the author's exact meaning, and his style is sometimes decidedly involved. The book, however, is obviously intended chiefly for the expert and the advanced student, who will no doubt be able successfully to interpret the rather unusual phraseology.

Über die Konstitution und Konfiguration von Verbindungen höherer Ordnung. ("On the Constitution and Configuration of Compounds of higher Order"). By Prof. Dr. ALFRED WERNER. Berlin: Julius Springer. 1914.

IN this lecture, which was delivered at Stockholm in 1913, Prof. Werner gave a résumé of his hypothesis concerning the arrangement of atoms in molecules. The

structure and space formulæ of the molecular compounds of cobalt, chromium, and platinum were briefly discussed, and a short account was given of the theory of principal and auxiliary valencies. The lecture gave an excellent sketch of Prof. Werner's views and of the work which has been done by himself and by other investigators in confirmation of them.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 8, February 23, 1914.

Preparation of Benzhydrol and of Symmetrical Tetraphenylethane.—Paul Sabatier and M. Murat.—To prepare benzhydrol either benzoic aldehyde or ethyl formate is allowed to act on phenyl magnesium bromide. The crystalline mass is treated with water acidified with sulphuric acid, the solution is saturated with sodium bicarbonate, the ethereal liquid decanted off, and the ether driven off by heating on the water-bath. On cooling crystals of nearly pure benzhydrol are deposited. If instead of driving off the ether the liquid is directly distilled, the chief product is symmetrical tetraphenyl ethane. When impure benzhydrol is distilled it rapidly decomposes owing to the catalysing action of the impurities, and this fact accounts for the formation of symmetrical tetraphenyl ethane. Pure fused benzhydrol, on the other hand, can be distilled at 298° under the ordinary pressure without undergoing any appreciable decomposition.

Verification of Laws of Transparence of Matter towards X-Rays.—Louis Benoit and Hippolyte Copaux.—The laws of transparence of matter towards X-rays show that transparence is essentially an atomic property. If the mass is equal per unit of surface exposed, and the quality of the rays is the same, the elements are less transparent the higher their atomic weights. The masses of equal transparence (equivalents of transparence) generally decrease as the atomic weights increase, and are represented by a well-defined curve. The authors have calculated the equivalents of transparence of three minerals, potassium ferrocyanide, cobaltic chloropentamine, and potassium silico molybdate, and have compared the results with the values obtained experimentally. The agreement between the two sets of numbers is very good, and thus the laws of transparence are confirmed.

Influence of Ethylenic Bond and of Carbonyl and Carboxyl Groups on the Absorption of Ultra-violet Rays.—Jean Bielecki and Victor Henri.—The characteristic band of carbonyl is influenced by the presence of a carboxyl or an ethylene bond in the molecule. In general, when a molecule contains two chromophores they mutually influence one another; if they are not too close in the molecule the result is an exaltation of the absorption—a hyperchromic effect. If the two chromophores are close together in the conjugate position there is more displacement of the characteristic bands of each chromophore towards the red, a hypsochromic effect.

Decomposition of Ammonia under the Action of Radium Emanation and Influence of Temperature upon Chemical Effects produced by Radiations of Radio-active Substances.—Eugène Wourzel.—Ammonia is decomposed by radium emanation into nitrogen and hydrogen, and no other reaction takes place. The quantity of gas evolved per unit of radiation destroyed increases with the pressure, but tends towards a certain limit. An increase of temperature favours the destruction of ammonia. Thus the number of cubic centimetres of ammonia destroyed per unit of radiation is nearly double at 108° and more than triple at 220° .

Bromination of Manganese in Ethereal Medium.—F. Ducelliez and A. Raynaud.—If bromine is added to

ether containing metallic manganese the ether which is first coloured red is gradually decolorised, and a semi-fluid orange deposit is formed. In presence of sulphuric acid this substance loses ether and forms crystals of formula $MnBr_2(C_2H_5)_2O$. When it is heated it yields white anhydrous $MnBr_2$. If the quantity of bromine in the original operation is greatly increased the deposit formed has the composition represented by the formula $MnBr_3(C_4H_{10}O)_3$.

Preparation of Pure Metals.—Maurice Billy.—Refractory metals such as titanium can be prepared by reducing their chlorides with hydrogen or sodium. In the former case a very high temperature is necessary, and it difficult to prevent oxidation if sodium is used. Both of these difficulties are avoided by the employment of sodium hydride. The reduction of the chlorides is complete at about 400° , the equation being $TiCl_4 + NaH = Ti + 4NaCl + 4H$. Vanadium tetrachloride can be reduced similarly. It is necessary to dry the metal in a current of CO_2 , for it catches fire in air spontaneously at 100° .

Etherification of Glycerin by Acetic Acid in Presence of Catalysts.—J. B. Senderens and Jean Aboulenc.—Potassium bisulphate acts catalytically in the etherification of glycerin by acetic acid, and anhydrous aluminium sulphate has a similar but stronger action. The results are still better when sulphuric acid is used as catalyst.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, April 21, at 3 o'clock, Dr. Walter Wahl will deliver the first of two lectures at the Royal Institution on "Problems of Physical Chemistry—(1) Study of Matter at High Pressures; (2) Study of Matter at Low Temperatures"; on Thursday, April 30, Dean Inge will begin a course of three lectures on "The Last Chapter of Greek Philosophy—Plotinus as Philosopher, Religious Teacher, and Mystic"; and on Saturday, April 25, Dr. T. E. Stanton commences a course of two lectures on "Similarity of Motion in Fluids—(1) The Theory of Similarity of Motion in Fluids and the Experimental Proof of its Existence; (2) The General Law of Surface Friction in Fluid Motion." The Friday Evening Discourse on April 24 will be delivered by Dr. Frank Watson Dyson (the Astronomer Royal) on "The Stars Around the North Pole," and on May 1 by Mr. E. F. Benson on "A Criticism on Critics."

The Institute of Metals.—*May Lecture.*—Prof. E. Heyn, of Berlin, one of the most famous scientists in Germany, is this year to deliver the annual May Lecture before the Institute of Metals. Prof. Heyn, who has made a life long study of the subject, has given the title of his discourse as "Internal Strains in Cold Wrought Metals, and some Troubles Caused Thereby." The Institute of Metals is fortunate in its May lecturers, and in the natural sequence of the subjects dealt with at these lectures. Thus, the last May Lecture, by Sir J. Alfred Ewing, K.C.B., F.R.S., was on the subject of "The Inner Structure of Simple Metals," and previously Dr. G. T. Beilby, F.R.S., had lectured on an allied subject, "The Hard and Soft States in Metals." Prof. Heyn's discourse will be given in the building of the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W., under the Chairmanship of Admiral Sir Henry Oram, K.C.B., F.R.S., the President of the Institute of Metals, on Tuesday, May 12, at 8.30 p.m. The Secretary of the Institute, Mr. G. SHAW SCOTT, M.Sc., of Caxton House, Westminster, S.W., will be glad to forward tickets to any readers who may desire to be present at the May Lecture.

Iron and Steel Institute.—The Annual Meeting of the Institute will be held in the new House of the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, May 7 and 8, 1914, commencing each day at 10.30 o'clock a.m.

Programme of Proceedings.

Thursday, May 7, at 10.30 a.m., General Meeting of Members; the Council will present their Report for the year 1913; the Hon. Treasurer will present the Statement of Accounts for 1913; Scrutineers will be appointed for the examination of voting papers for election of new Members of the Institute; the retiring President (Mr. Arthur Cooper) will induct into the Chair the President-elect (Mr. Adolphe Greiner); the Bessemer Gold Medal for 1914 will be presented to Mr. Edward Riley, F.I.C.; the President will deliver his Inaugural Address; a selection of papers will be read and discussed (Nos. 16, 10, 8); papers Nos. 5, 12, 15 will be read and discussed as far as time permits. At 7.0 p.m., Annual Dinner of the Institute at the Connaught Rooms, Great Queen Street, W.C.

Friday, May 8, at 10.30 a.m., General Meeting of Members; the Andrew Carnegie Gold Medal (for 1913) will be presented to Mr. Thomas Swinden, D.Met., and the award of Research Scholarships for the current year will be announced; papers Nos. 14, 9, 11 will be read and discussed; if time permits other papers may be discussed at any of the Sessions, in which case due notice will be given. Those papers for which time cannot be found will be taken as read and discussed by correspondence.

The following is the list of papers that are expected to be submitted for reading and discussion:—

1. J. O. Arnold, D.Met., F.R.S., and G. R. Bolsover: "Forms in which Sulphides may Exist in Steel Ingots."
2. C. Benedicks, Ph.D.: "Experiments on Allotropy of Iron (Behaviour of Ferromagnetic Mixtures; Dilatation of Pure Iron)."
3. A. Bose: "Recent Developments of the Iron and Steel Industry in India."
4. C. Chappell: "The Re-crystallisation of Deformed Iron."
5. C. A. Edwards, D.Sc., and H. C. H. Carpenter, Ph.D.: "The Hardening of Metals, with Special Reference to Iron and Its Alloys."
6. J. N. Friend, D.Sc., and C. W. Marshall: "Influence of Molybdenum upon the Corrosibility of Steel."
7. H. C. Greenwood, D.Sc.: "Note on a Curious Case of Decarburisation during the Hardening of Steel Dies."
8. Sir Robert A. Hadfield, F.R.S., and B. Hopkinson, F.R.S.: "The Magnetic and Mechanical Properties of Manganese Steels."
9. H. L. Heathcote, B.Sc.: "Some Improvements in Case-hardening Practice."
10. S. A. Houghton: "Failures of Heavy Boiler Shell Plates."
11. E. Humbert and A. Hethey, B.Sc.: "Production of Steel Direct from the Ore."
12. A. McCance, B.Sc.: "Theory of Hardening."
13. M. Misson: "The Colorimetric Estimation of Sulphur in Pig Iron and Steels by means of Paper Impregnated with a Solution of Arsenious Anhydride in Hydrochloric Acid."
14. F. Müller: "The Development of Dry Cleaning in Blast-furnace Gas Purification."
15. W. Rosenhain, D.Sc., F.R.S., and J. L. Haughton, M.Sc.: "A new Reagent for Etching Mild Steel."
16. F. Schuster, D.Ing.: "Results of Talbot Process at Witkowitz."

MEETINGS FOR THE WEEK.

TUESDAY, 21st.—Royal Institution, 3. "Problems of Physical Chemistry," by W. Wahl, Ph.D.

WEDNESDAY, 22nd.—Faraday Society, 8. "Recording Pyrometers," by C. R. Darling. "Embrittling of Iron by Caustic Soda," by J. H. Andrew. "Diffusion and Membrane Potentials," by E. B. R. Prideaux. "Acidic and Colloidal Properties of Aluminium Hydroxide," by R. E. Slade and W. G. Polack. "On 'Negative' Adsorption," by A. M. Williams.

FRIDAY, 24th.—Royal Institution, 9. "The Stars around the North Pole," by F. W. Dyson, F.R.S., &c.

SATURDAY, 25th.—Royal Institution, 3. "Similarity of Motion in Fluids," by T. E. Stanton, D.Sc., &c.

THE CHEMICAL NEWS

VOL. CIX., No. 2839.

A FURTHER EXPERIMENT ON THE COLOUR OF COBALT SALTS IN SOLUTION.

By J. E. MARSH.

WHEN a pink solution of cobalt and sodium chloride in a mixture of water and acetone is subjected to an electric current a blue layer collects at the anode. A solution containing 1 part by weight of sodium chloride, 2 of cobalt chloride $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 8 of acetone, and 8 of water was placed in a U-tube. The town current of about 100 volts with lamp resistance was passed through by means of carbon terminals. The light blue layer collected at the anode, the rest of the solution retaining its pink colour. On reversing the current the blue layer was decolorised at what was now the cathode and another blue layer appeared in the other limb of the tube. The U-tube should be cooled externally, otherwise, owing to the heating effect of the current, the blue layer may appear temporarily in both limbs of the tube. The experiment illustrates very well the electro-negative character of the blue cobalt complex; the solution at the anode becomes supersaturated, with separation of the blue acetone layer. When a solution of cobalt chloride alone in water and acetone was treated in the same manner metallic cobalt separated at the cathode, and no separation into layers was observed.

UNUSUAL DOLOMITES

By NICHOLAS KNIGHT.

THE rock formation of North-east Iowa belongs to the Niagara period and is dolomitic in character. The various layers show slight differences, but on the whole they are typical dolomites, having the formula $\text{CaCO}_3, \text{MgCO}_3$. The analysis of a fair sample shows:—

	Per cent.
CaCO_3	54.35
MgCO_3	43.65
SiO_2	1.00
Fe_2O_3 and Al_2O_3	1.00
Total	100.00

About a year ago our attention was called to a peculiar dolomite from the Simplon Tunnel reported by Gabriele Lincio (*Reale Accademia delle Scienze di Torino*, 1911). On analysis the specimen was found to have the formula $3\text{CaCO}_3, 2\text{MgCO}_3, \text{FeCO}_3$, and so is called a ferri-ferous dolomite.

At our suggestion Mr. C. B. Smith analysed specimens from a number of different layers of the dolomite rock in Mount Vernon, Iowa, and vicinity. He found a peculiar looking specimen at the "Palisades," on the Cedar River, about six miles from Mount Vernon. The specimen is coarse granular, pinkish to reddish brown, resembling iron rust, with white crystals disseminated through it. It is quite a deep red in certain portions. The specimen occurs in pockets in the regular dolomite rock. The analysis by Mr. Smith resulted as follows:—

	Per cent.
CaCO_3	64.50
MgCO_3	33.87
SiO_2	0.57
Fe_2O_3 and Al_2O_3	0.96
Total	99.90

The analysis did not show the amount of iron that the appearance of the rock led us to expect. The figures correspond quite closely to the formula $3\text{CaCO}_3, 2\text{MgCO}_3$, the iron alumina and silica replacing the equivalent amount of magnesium carbonate.

Other specimens from the same locality that seemed to differ in appearance from the typical layers resulted as follows:—

	(Per cent.)
(1) CaCO_3	52.81
MgCO_3	46.15
SiO_2	0.37
Fe_2O_3 and Al_2O_3	0.68
Total	100.01
(2) CaCO_3	51.52
MgCO_3	47.06
SiO_2	0.53
Fe_2O_3 and Al_2O_3	0.58
Total	100.01

The analyses show the small amounts of silica, iron, and alumina; these three constituents aggregate about 1 per cent.

Attention has been called to another iron-bearing dolomite from the Simplon Tunnel by Mario Delgrosso (*Riv. Min. Crist. Ital.*, xli., 56–64). This differs from all the foregoing specimens. The analysis leads to the formula $4\text{CaCO}_3, 3\text{MgCO}_3, (\text{Fe}, \text{Mn})\text{CO}_3$.

O. Kallauner (*Chem. Zeit.*, xxxvii., 1317) has studied the thermal dissociation of normal dolomite. He found that dissociation into the two constituents, CaCO_3 and MgCO_3 , begins at 500° and reaches a maximum between 710° and 730° . At higher temperatures the MgCO_3 and CaCO_3 dissociate.

It might prove interesting and instructive to study the thermal dissociation of some of the abnormal specimens.

Cornell College, April 1, 1914.

SIMPLE AND COMPLEX ROTATORY DISPERSION.*

By T. MARTIN LOWRY and T. W. DICKSON.

THE object of the present paper is to discuss the form of the curves of rotatory dispersion in the light of experimental evidence obtained in a series of recent investigations. Some of these have already been published, whilst others are still awaiting completion. (Lowry, *Proc. Roy. Soc.*, 1908, A. lxxxi., 472; *Phil. Trans.*, 1912, A. ccxii., 261; *Trans. Chem. Soc.*, 1913, ciii., 1062. Lowry and Dickson, *Ibid.* 1067. Lowry, *Ibid.* 1322; *Trans. Chem. Soc.*, 1914, cv., 81. Lowry, Pickard and Kenyon, *Ibid.* 94. Lowry and Dickson, *Proc. Chem. Soc.*, June 5, 1913).

The experiments cover all the different varieties of optical rotation, namely: (1) the natural rotations observed in crystals of quartz, and (2) the artificial rotatory power produced by placing it in a magnetic field, (3) and (4) the optical and magnetic rotation in optically-active liquids such as *sec*-butyl alcohol and its homologues. The experiments include observations in the ultra violet and infra-red, as well as in the visible region of the spectrum.

A. Rotatory Dispersion in Quartz.

The only data which will permit a rigid test of the form of the curve of rotatory dispersion are those which have been obtained in the case of quartz. Whereas, in the case of other substances, it is very rarely practicable to obtain readings as large as 100° , it has been found possible

* A Contribution to a General Discussion on "Optical Rotatory Power," held before the Faraday Society, March 27, 1914

in the case of quartz to record an *observed* rotation exceeding 100,000°. In the visible region of the spectrum, readings can be taken to seven significant figures, with errors of observation amounting to only a few parts per million. The readings can be extended into the ultra-violet, at least as far as wave-length 2200 A.U., and at least as far as wave-length 20,000 A.U. in the infra-red. In the ultra-violet the readings can be taken without difficulty to 1°, and it would not be difficult, by mere perseverance, to reduce the errors of observation to about 0.1°. As the readings are larger than in the visible spectrum, the errors of observation are, relatively, not much greater; indeed, if attention be paid to the fact that the photographic observations are made on narrow spectrum-lines, whilst the visible readings are taken with wide blocks of light, the greater spectral purity of the ultra-violet readings may impart to them a higher degree of accuracy than that actually attained by visual observation. The infra-red readings are necessarily of a lower order of accuracy, but are of great value on account of the wide range of wave lengths which they cover.

The first formula for the rotatory dispersion of light in quartz was given by Biot, who suggested that—

$$\alpha = \frac{k}{\lambda^2} \quad \dots \quad (1)$$

The rotation produced in light of any colour being inversely proportional to the square of the wave-length. Boltzmann gave the equation—

$$\alpha = \frac{k_1}{\lambda^2} + \frac{k_2}{\lambda^4} + \frac{k_3}{\lambda^6} + \dots \quad (2)$$

corresponding closely with the Cauchy formula for refractive indices. Drude ("Theory of Optics," 1917, p. 413) suggested a general equation—

$$\alpha = \frac{k_n}{\lambda^2 - \lambda_n^2} \quad \dots \quad (3)$$

this equation, if $\lambda > \lambda_n$, can be expanded into a series of the same type as Boltzmann's equation (2).

In Drude's equation the constants λ_n are the wave-lengths *in vacuo* of light having the same periods as the natural periods of free vibration of the "ions" or "electrons" by which the optical properties of the molecule are determined. In the case of quartz the values of these constants have been deduced from measurements of refractive power as follows—

$$\begin{aligned}\lambda_1^2 &= 0.010627 \mu^2 \\ \lambda_2^2 &= 78.22 \mu^2 \\ \lambda_3^2 &= 430.6 \mu^2.\end{aligned}$$

Drude assumed that these refraction-data could be used to determine the course of the curve of rotatory dispersion. He therefore wrote the equation in the form—

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda^2 - \lambda_2^2} + \frac{k_3}{\lambda^2 - \lambda_3^2} + \frac{k'}{\lambda^2} \quad \dots \quad (4)$$

and calculated the values of k_1 , k_2 , k_3 , &c., from existing data for the rotatory power of quartz over the range from 21,400 A.U. (2140 μ) to 2193.5 A.U. (0.21935 μ). He found $k_2 = k_3 = 0$, and concluded (i.) "that the kinds of ions whose natural periods lie in the ultra-red are inactive." On the other hand, he had already adopted the view that quartz has ions for which λ_n is much smaller than the wave-length of light, and concluded (ii.) "that the activity coefficient k' of ions of this kind, for which λ^2 may be neglected in comparison with λ_2^2 , must be taken into consideration." By throwing the equation into the form—

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_2^2} + \frac{k'}{\lambda^2} \quad \dots \quad (5)$$

where $\lambda_2^2 = 0.010627$, $k_1 = 12.200$, $k' = -5.046$, Drude was able to calculate the rotatory power of quartz over the whole range with an average error of 0.060° per mm. in a series of 18 observations.

The more accurate measurements put forward in 1912 could not be represented, even in the narrow range of the visible spectrum, by Drude's simplified equation (5). In order to secure a reasonable concordance between the observed and calculated values, it was necessary to go back upon Drude's first conclusion and to restore an infra-red term to the equation, which thus became—

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_2^2} + \frac{k_2}{\lambda - \lambda_2^2} + \frac{k'}{\lambda^2} \quad \dots \quad (6)$$

This formula gave results which were a great improvement on the figures quoted by Drude, the average discrepancy in the visible region of the spectrum being reduced from 0.038 to 0.001° per mm.

Further measurements in the ultra-violet region, which are not yet available for publication, show that even this improved formula becomes grossly inaccurate when carried out towards the limit of transmission of light by quartz. It cannot be made to give good results so long as the values of λ_1^2 and λ_2^2 deduced from the refraction data are used as constants in the equation, thus limiting the number of arbitrary constants to three. The value of the infra-red term is not important, as it comes into the equation as a quantity that remains almost constant over a wide range of the spectrum; there is therefore no objection to retaining the value of λ_2^2 deduced from the refractive power of the crystal in the extreme infra-red. But there is good reason to think that the value of λ_1^2 has been given incorrectly, and that the value of this constant may be deduced with much greater accuracy from exact observations of rotatory dispersion than from measurements of refractive power.

It is impossible at present to state the final form of the equation, but a very satisfactory agreement can be obtained over the whole range from w.l. 16,740 to w.l. 2327 by using Drude's general equation with *three* terms, namely, one infra-red term and two ultra-violet terms, thus—

$$\alpha = \frac{k_0}{\lambda^2 - \lambda_0^2} + \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda^2 - \lambda_2^2} \quad \dots \quad (7)$$

In this equation $\lambda_2^2 = 78.22$ as before; λ_1^2 is a constant differing somewhat from the value 0.010627 given by Drude; λ_0^2 represents another wave length in a remote part of the inaccessible ultra-violet region. Its magnitude is not negligible as Drude supposed, but is so small that the "probable error" as determined from the incomplete data at present available was found to be larger than the number itself. An equally good agreement can, however, be reached by replacing the whole of the infra-red term by a constant, putting $\lambda_0^2 = 0$, and regarding λ_1^2 as an unknown quantity. The equation then becomes—

$$\alpha = \frac{k_0}{\lambda^2} + \frac{k_1}{\lambda^2 - \lambda_1^2} + k_2 \quad \dots \quad (8)$$

This equation contains four arbitrary constants, as compared with the three arbitrary constants of equation (6) and the five arbitrary constants of equation (7). This number of constants appears to be quite sufficient to express the data at present available, and, from the empirical point of view, affords the most satisfactory solution of the problem of reducing the data to algebraic form.

B. Optical and Magnetic Rotatory Dispersion in Simple Organic Liquids.

In the case of a large number of simple organic liquids, the optical and magnetic rotatory dispersion may be expressed by the equation—

$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2} \quad \dots \quad (9)$$

Thus the average values of the *magnetic* dispersion-ratios in a series of 25 substances have been found to compare with the calculated values as follows :—

	Li 6708.	Cd 6438.	Na 5893.	Hg 5461.	Cd 5086.	Cd 4800.	Hg 4359.
Obs.	0.647	0.705	0.850	1.000	1.164	1.321	1.636
Calc.	0.647	0.705	0.850	1.000	1.166	1.322	1.636

In the case of the optical rotatory power of phenyl-methylcarbinol, $C_6H_5.CH(OH).CH_3$, the figures are:—

Obs.	0.629	0.687	0.839	1.000	1.184	1.361	1.736
Calc.	0.627	0.686	0.839	1.000	1.183	1.362	1.735

These figures show that the simple formula is sufficient to express the course of the curves of optical and magnetic rotatory dispersion within the limits of the visible spectrum.*

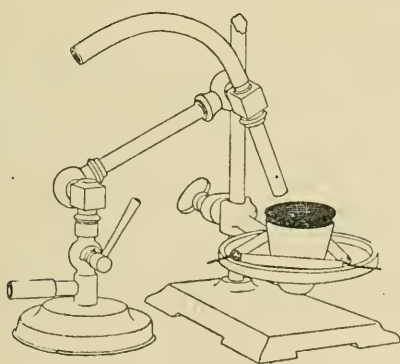
This does not prove that the substances in question are characterised by only one natural period of free vibration. Even in the case of quartz, which is known to possess four such natural periods, the optical rotatory power can be represented within the same limits of accuracy by the simple formula. But, until the methods of measurements have been developed to an extent which is now quite impracticable, the simple formula will hold its own, as the only possible way of expressing the experimental data in the case of simple organic liquids.

(To be continued).

THE PURIFICATION OF BARIUM SULPHATE PRECIPITATED IN THE DETERMINATION OF BARIUM.

By F. A. GOOCH and D. U. HILL.

WHEN in the determination of barium as the sulphate the precipitation is made in the presence of alkali salts, considerable errors—sometimes as much as 20 mgrms. in one half gm. of precipitate—may be occasioned by occlusion of the foreign salts. It has been found that upon dissolving the precipitate of barium sulphate in concentrated sulphuric acid and evaporating to dryness, the barium sulphate crystallises in more or less coarsely granular crystals which may be washed free from the other sul-



phates (Mar, *Am. Journ. Sci.*, 1891, xli., 295). The evaporation must be made with special care in order to avoid loss by spattering and creeping. With a ring burner this process takes several hours, but with a Hempel burner an evaporation can be made safely in about one half-hour. The present object has been to find out whether the evaporation cannot be safely made by directing the flame of a blast lamp down upon the surface of the liquid, thus

substituting for the Hempel burner a piece of apparatus that is in more general use.

Preliminary experiments to determine whether an evaporation without loss of barium sulphate could be made with the blast lamp were carried out in the following manner:—Crystallised barium chloride (chemically pure) was powdered and bottled without drying, and the water content determined by gentle ignition. Of this salt portions of 0.5000 gm. each were weighed into a previously weighed platinum crucible. About 5 cc. of water was added, and then from 2 cc. to 5 cc. of sulphuric acid. The water and excess of sulphuric acid were evaporated off by directing a small flame from the blast lamp nearly vertically downward upon the liquid. The evaporation required about fifteen minutes. The results obtained upon weighing the crucible and barium sulphate were satisfactory in three cases out of five, but in the other two cases there was loss. To prevent this a cone of fine platinum gauze was fitted into the mouth of the crucible and the flame was directed against the point of the cone. This prevented the loss by spattering. The point of the cone must not be allowed to dip into the liquid, for otherwise some of the barium sulphate will be left above the gauze and may be blown away. The gauze was weighed with the crucible and cover each time, so that if any of the barium sulphate should spatter against the gauze its weight would not be lost. The results where the gauze was used were more consistently satisfactory, and we felt encouraged to carry on further experiments using the gauze, but not without it. The average time required for completing an evaporation in these and subsequent experiments where the gauze was used was about one half-hour. Table I. gives the results of the experiments in which the naked flame was directed upon the solution, Table II. those of the experiments in which the gauze was interposed.

TABLE I.

Wt. of $BaCl_2 \cdot 2H_2O$ taken. Gm.	$BaSO_4$ found. Gm.	$BaSO_4$ by theory. Gm.	Error. Gm.
0.4996	0.4744	0.4773	+0.0001
0.4996	0.4774	0.4773	+0.0001
0.4996	0.4747	0.4773	-0.0026
0.4996	0.4773	0.4773	0.0000
0.4996	0.4765	0.4773	-0.0008

TABLE II.

0.4996	0.4770	0.4773	--0.0003 (a)
0.4996	0.4777	0.4773	+0.0004
0.4996	0.4768	0.4773	-0.0005
0.4996	0.4768	0.4773	-0.0005
0.4996	0.4774	0.4773	+0.0001
0.4996	0.4776	0.4773	+0.0003

(a) The tip of the gauze dipped into the liquid.

For use in the subsequent experiments a solution to contain approximately 0.5 gm. of $BaCl_2 \cdot 2H_2O$ in 50 cc. was prepared by weighing out 20 grms. of the $BaCl_2 \cdot 2H_2O$, transferring it to a 2-litre measuring flask, and filling the flask to the mark with distilled water. The quantity of the solution used in each experiment was determined by drawing portions of 50 cc. from a burette into previously weighed glass-stoppered Erlenmeyer flasks and weighing. Since 0.01 gm. of the solution contained only 0.0001 gm. of $BaCl_2 \cdot 2H_2O$, it was not necessary to weigh more accurately than to 1 centigram. However, the weighing was usually made to a milligram.

In the first series of experiments determinations of barium in the absence of salts of other metals were made in the usual manner, and the effect of the treatment of the precipitate of barium sulphate with sulphuric acid in the way described was tried. The procedure in detail was as follows:—One cubic centimetre of strong sulphuric acid was added to 100 cc. of water in a 250 or 350 cc. beaker, and the mixture was heated to boiling. The weighed amount of barium chloride solution was washed from the

* Additional evidence in reference to the optical rotatory power of α -methylglucoside is given in another paper (Lowry and Abram, p. 171).

Erlenmeyer flask into the hot acid solution. The beaker was then allowed to stand on the steam-bath for a few hours, and in most cases at least one night intervened between the precipitating and the filtering of the material. The precipitate was filtered on ashless paper (ash 0.00011 grm.) without using pressure, ignited with the paper in a weighed platinum crucible, and brought to constant weight with a Bunsen burner. From 2 to 5 cc. of sulphuric acid were then added, the gauze cone fitted in the crucible, the evaporation made as in the previously described experiments, and the crucible with its contents, the gauze, and cover, weighed. Only a trifling change of weight would be expected, since the only solid material that could be occluded in the original precipitate is barium chloride. As this would take the place of an equivalent amount of the sulphate, and the molecular weights of the chloride and sulphate do not differ greatly, no very great error could be introduced in this way. In the reverse process—the determination of sulphate by precipitation with excess of barium chloride—"the occlusion of barium chloride in the precipitate of barium sulphate may lead to very serious error" (Richards and Parker, *Proc. Am. Acad. Sci.*, xxxi., 76). Table III. gives the results of the experiments just described, corrected for the filter-ash, 0.0001 grm.

In the next series of experiments, 10 cc. portions of a 20 per cent solution of potassium chloride were added to the 100 cc. of water and the 1 cc. of sulphuric acid before the precipitation was made. The procedure just described was then followed to the point where the evaporation with sulphuric acid was completed. The material was then washed from the crucible on to a filter-paper and washed thoroughly to remove the potassium sulphate. The filter was dried and ignited in the crucible, and the crucible and contents brought to constant weight. Table IV. gives the results of this series. Correction has been made for the weight of the ash (0.0001 grm.) of the second filter-paper, that of the first paper having been dissolved presumably by the treatment with sulphuric acid.

TABLE III.

BaSO ₄ found.		Results reduced to 50 grms. of solution.			Error.
Weight of BaCl ₂ solution used.	Before treatment.	After treatment.	BaSO ₄ before treatment.	BaSO ₄ after treatment.	
Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
50.281	0.4767	0.4766	0.4740	0.4739	+0.0002
50.348	0.4784	0.4771	0.4751	0.4738	+0.0001
50.199	0.4764	0.4754	0.4745	0.4735	-0.0002
50.293	0.4786	0.4765	0.4758	0.4737	0.0000

TABLE IV.

Weight of BaCl ₂ solution used.	Before treatment.	After treatment.	BaSO ₄ before treatment.	BaSO ₄ after treatment.	BaSO ₄ by theory.	Error.
Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
50.262	0.4814	0.4749	0.4789	0.4724	0.4737	-0.0013
50.171	0.4870	0.4772	0.4854	0.4756	0.4737	+0.0019
50.281	0.4804	0.4759	0.4777	0.4732	0.4737	-0.0005
50.285	0.4838	0.4762	0.4810	0.4735	0.4737	-0.0002
50.330	0.4805	0.4755	0.4774	0.4724	0.4737	-0.0013
50.320	0.4818	0.4766	0.4787	0.4736	0.4737	-0.0001
50.278	0.4813	0.4765	0.4786	0.4738	0.4737	+0.0001
50.301	0.4804	0.4751	0.4775	0.4723	0.4737	-0.0014*
50.274	0.4797	0.4762	0.4771	0.4736	0.4737	-0.0001
50.235	0.4790	0.4753	0.4768	0.4731	0.4737	-0.0006

Average... 0.4789 0.4733

* A slight loss by creeping was expected in this experiment.

This investigation shows that the evaporation can be carried out successfully with the use of the blast lamp and platinum gauze as a substitute for the Hempel burner, and that, although the accuracy of the results is not as great as could be wished, yet, where alkali salts are present, this method of purification reduces the otherwise very large error to a value at most not more than 1 or 2 mgrms. for half-a-grm. of barium sulphate.—*American Journal of Science*, xxxv., p. 311.

ERRORS IN GAS ANALYSIS DUE TO ASSUMING THAT THE MOLECULAR VOLUMES OF ALL GASES ARE ALIKE.*

By GEORGE A. BURRELL and FRANK M. SEIBERT.

(Concluded from p. 189).

Recent Specific Gravity and Molecular Volume Determinations.

RECENT specific gravity determinations (at 0° C. and 760 mm. pressure) for different gases and of the molecular volumes of carbon dioxide and ethane at various partial pressures are presented in Table III. (H. Landolt and R. Börnstein, "Physikalisch-Chemische Tabellen," 1912, p. 148).

TABLE III.—Results of Specific Gravity Determinations of Various Gases.

Gas.	Molecular weight.	Specific gravity (Air=1).		Observer.	Theoretical Observed.
		Theoretical.	Observed.		
CH ₄	16.03	0.5538	0.5545	Baumé and Perrot	0.999
C ₂ H ₆	30.05	1.0381	1.0494	Baumé and Perrot	0.990
CO	28.00	0.9673	0.9670	Leduc	1.000
CO	28.00	0.9673	0.9672	Rayleigh	1.000
CO ₂	44.00	1.5201	1.5287	Leduc	0.994
CO ₂	44.00	1.5201	1.5291	Rayleigh	0.994
N ₂	28.02	0.9680	0.9674	Rayleigh	1.001
N ₂	28.02	0.9680	0.9672	Leduc	1.001
O ₂	32.00	1.1055	1.1054	Rayleigh	1.000
O ₂	32.00	1.1055	1.1052	Leduc	1.000
C ₂ H ₄	28.03	0.9683	0.9852	Saussure	0.983
C ₂ H ₂	26.02	0.8989	0.9056	Leduc	0.992

TABLE IV.—Molecular Volumes of Carbon Dioxide at 20° C. and Various Partial Pressures.

Pressure. Mm.	Molecular volume.	Percentage of total pressure.
100	0.999	13.1
200	0.999	26.3
300	0.998	39.5
400	0.997	52.6
500	0.997	65.8
600	0.996	78.9
700	0.995	91.9
760	0.995	100.0

In compiling the table of molecular volumes of carbon dioxide (Table IV.), advantage was taken of the work of Rayleigh and Chappuis (see Note) on the coefficient of expansion of carbon dioxide. The specific gravity of carbon dioxide as given by Rayleigh was determined at 0° C. and 760 mm. pressure. The value at 20° C. and 760 mm. pressure was determined from the coefficient of expansion of carbon dioxide between 0° C. and 20° C.

(NOTE.—Rayleigh, "On the Densities of Carbonic Oxide, Carbonic Anhydride, and Nitrous Oxide," *Proc. Roy. Soc.*, 1897, lxii., 204; "On the Compressibility of Gases between One Atmosphere and Half an Atmosphere of Pressure," *Trans. Roy. Soc.*, 1905, cciv., 360. P. Chappuis, *Bull. Inst. Poids et Mes.*, 1903, xiii., 190).

TABLE V.—Molecular Volumes of Ethane at 0° C. and Various Partial Pressures.

Pressure (mm.).	Molecular volume.
100	0.999
200	0.997
300	0.996
400	0.995
500	0.994
600	0.992
700	0.991
760	0.990

* Technical Paper 54, Department of the Interior, U.S.A. Bureau of Mines.

TABLE VI.—Results of Analyses of Methane from Different Sources.

	Mine gas. Laboratory No.—					Methane prepared by method of Gladstone and Tribe.			Natural gas. Laboratory No.—	
	1986.	2492.	2781.	2990.	2481.	Sample 1.	Sample 2.	Sample 3.	3150.	3149.
Volume of sample taken (cc.)..	33'70	45'75	38'70	42'30	43'70	42'00	31'40	47'15	41'70	40'40
Volume after carbon dioxide absorption (cc.)	33'70	45'75	38'70	42'30	43'70	41'95	31'40	47'15	41'70	38'40
Portion taken (cc.)	33'70	45'75	38'70	42'30	43'70	41'95	31'40	47'15	41'70	38'40
Oxygen added (cc.)	95'65	70'10	68'05	51'10	40'90	99'10	71'25	99'45	87'40	80'00
Total volume (cc.)	129'35	115'85	106'75	93'40	90'60	141'05	102'65	146'60	129'10	118'40
Volume after burning (cc.) ..	65'80	58'95	83'20	67'20	56'80	59'50	40'85	53'85	60'05	56'05
Contraction (cc.)	63'55	56'90	23'55	26'20	33'80	81'55	61'80	92'75	69'05	62'35
Volume after absorption of carbon dioxide (cc.)	34'30	30'65	71'40	54'15	39'90	18'90	10'15	7'90	25'75	25'05
Carbon dioxide (cc.).. .. .	31'50	28'30	11'80	13'05	16'90	40'60	30'70	45'95	34'30	31'00
Carbon dioxide (percentage of total pressure)	47'9	47'9	14'2	19'4	29'7	68'2	75'1	85'3	57'1	55'3
Molecular volume of carbon dioxide corrected from—										
Table IV.	0'997	0'997	—	—	—	0'997	0'996	0'996	0'997	0'997
Theoretical equation, one-half contraction minus carbon dioxide (cc.) ..	0'28	0'15	-0'02	0'05	0'0	0'18	0'20	0'43	0'22	0'18
Corrected equation; correction times contraction minus correction times carbon dioxide (cc.) ..	0'12	0'01	—	—	—	-0'03	+0'02	0'15	+0'05	0'02
Methane from uncorrected contraction (per cent)	94'3	62'2	30'5	31'0	38'7	97'1	98'4	98'4	82'8	77'2
Methane from uncorrected carbon dioxide (per cent)	93'5	61'9	30'5	30'9	38'7	96'7	97'8	97'5	82'3	76'7
Difference (per cent)	0'80	0'30	0'0	0'10	0'0	0'4	0'6	0'9	0'5	0'5
Methane from corrected contraction (per cent)	94'1	62'0	—	—	—	96'90	98'2	98'2	82'60	77'0
Methane from corrected carbon dioxide (per cent)	93'8	62'0	—	—	—	97'0	98'2	97'9	82'5	77'0
Difference (per cent)	0'30	0'0	—	—	—	0'10	0'0	0'3	0'10	0'00

TABLE VII.—Analyses of Carbon Monoxide Mixed with Air.
(Prepared by the action of concentrated sulphuric acid on oxalic acid).

	Sample 1.	Sample 2.	Sample 3.	Sample 4.	Sample 5.
Volume of sample taken (cc.)	50'95	31'50	52'95	51'20	54'25
Oxygen added (cc.)	39'50	77'90	35'40	36'15	47'40
Total volume (cc.)	90'45	109'40	88'35	87'35	101'65
Volume after burning (cc.)	66'10	94'40	62'95	62'60	75'60
Contraction (cc.)	24'35	15'00	25'40	24'75	26'05
Volume after absorption of carbon dioxide (cc.)	17'80	64'40	12'75	13'85	23'90
Carbon dioxide (cc.)	48'30	30'00	50'20	48'75	51'70
Carbon dioxide (percentage of total pressure)	73'1	31'8	79'7	77'8	68'4
Molecular volume of carbon dioxide corrected from—					
Table IV.	0'997	—	0'996	0'996	0'997
Theoretical equation (two times contraction minus carbon dioxide)	0'40	0'00	0'60	0'75	0'40
Corrected equation (correction times contraction minus correction times carbon dioxide)	-0'04	0'00	-0'01	+0'15	-0'07
Carbon monoxide from uncorrected contraction (per cent)	95'6	95'2	95'9	96'7	96'0
Carbon monoxide from uncorrected carbon dioxide (per cent)	94'8	95'2	94'8	95'2	95'3
Difference (per cent)	0'8	0'0	1'1	1'5	0'7
Carbon monoxide from corrected contraction (per cent)	95'1	—	95'2	95'9	95'5
Carbon monoxide from corrected carbon dioxide (per cent)	95'0	—	95'2	95'6	95'6
Difference (per cent)	0'1	—	0'0	0'3	-0'1

The graph was plotted from two values determined experimentally, the value at 20° C. and 760 mm. pressure and that at 20° C. and 380 mm. pressure.

Table V. gives the molecular volumes of ethane at 0° C. and various partial pressures.

The coefficient of expansion of ethane between 0° C. and 20° C. has not been determined; consequently the same molecular volume was used at 20° C., the ordinary laboratory temperature, as was determined by Baumé and Perrot at 0° C. The resulting error can be disregarded without introducing any appreciable error in the analysis, judging

from the case of the molecular volume of carbon dioxide which at 20° C. is only 0'001 different from the value at 0° C.

The values between 0'0 and 760 mm. pressure are interpolated from the values at 0'0 mm. and 760 mm., which were determined experimentally.

From a careful search of the literature, the authors were unable to find any determination of the density of propane, but they have information at hand that shows beyond doubt that, at 0° C. and 760 mm. pressure, propane is by no means a perfect gas.

Following are some equations that hold only when the partial pressure of the combustible gas and that of the carbon dioxide (at 0° and 760 mm.) produced by the combustion are 95 to 100 per cent of the total pressure. If the partial pressures differ from these, different molecular volumes, depending upon the partial pressures, are used.

Theoretical and Corrected Equations for Combustion of certain Gases.

CH_4 , Theoretical Equation: $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$.

CH_4 , Corrected Equation: $0.999\text{CH}_4 + 2.000\text{O}_2 = 0.994\text{CO}_2 + 2\text{H}_2\text{O}$. 0.999 volumes + 2.000 volumes - 0.994 volumes = 2.005 volumes = contraction.

0.498 contraction = CH_4 $1.005\text{CO}_2 = \text{CH}_4$

C_2H_6 , Theoretical Equation: $\text{C}_2\text{H}_6 + 3.5\text{O}_2 = 2\text{CO}_2 + 3\text{H}_2\text{O}$.

C_2H_6 , Corrected Equation: $0.990\text{C}_2\text{H}_6 + 3.5\text{O}_2 = 1.988\text{CO}_2 + 3\text{H}_2\text{O}$. 0.990 volumes + 3.5 volumes - 1.988 volumes = 2.502 volumes = contraction.

0.396 contraction = C_2H_6 $0.497\text{CO}_2 = \text{C}_2\text{H}_6$

CO , Theoretical Equation, $2\text{CO} + \text{O}_2 = 2\text{CO}_2$.

CO , Corrected Equation: $2.000\text{CO} + 1.000\text{O}_2 = 1.988\text{CO}_2$. 2.000 volumes + 1.000 volumes - 1.988 volumes = 1.012 volumes = contraction.

1.976 contraction = CO $1.006\text{CO}_2 = \text{CO}$

C_3H_8 , Theoretical Equation: $\text{C}_3\text{H}_8 + 5\text{O}_2 = 3\text{CO}_2 + 4\text{H}_2\text{O}$.

C_3H_8 , Corrected Equation: The observed density of propane, as far as the authors were able to determine, has never been published.

C_2H_4 , Theoretical Equation: $\text{C}_2\text{H}_4 + 3\text{O}_2 = 2\text{CO}_2 + 2\text{H}_2\text{O}$.

C_2H_4 , Corrected Equation: $0.983\text{C}_2\text{H}_4 + 3.000\text{O}_2 = 1.988\text{CO}_2$. 0.983 volumes + 3.000 volumes - 1.988 volumes = 1.995 volumes = contraction.

0.493 contraction = C_2H_4 $0.494\text{CO}_2 = \text{C}_2\text{H}_4$

C_2H_2 , Theoretical Equation: $\text{C}_2\text{H}_2 + 2.5\text{O}_2 = 2\text{CO}_2 + \text{H}_2\text{O}$.

C_2H_2 , Corrected Equation: $0.992\text{C}_2\text{H}_2 + 2.500\text{O}_2 = 1.988\text{CO}_2 + \text{H}_2\text{O}$. 0.992 volumes + 2.500 volumes - 1.988 volumes = 1.504 volumes = contraction.

0.659 contraction = C_2H_2 $0.499\text{CO}_2 = \text{C}_2\text{H}_2$

Gas Analysis Apparatus used by the Authors.

The apparatus used by the authors for the analysis of natural gas and other combustible gases is shown in Fig. 1.

It consists of a 100 cc. burette, which is graduated in tenths of 1 cc., but can easily be read to 0.05 cc. Mercury is used as the trapping fluid. At *f* is the compensating tube. Both the burette and the compensating tube are contained in a water-jacket. At *g* is a mercury manometer.

Attached to the burette by means of rubber tubing is the train of stopcocks which are in turn connected to the caustic potash pipette *a*, the alkaline pyrogallate or phosphorous pipette *b*, the slow combustion pipette *c*, and the alkaline pyrogallate pipette *d*, which contains a supply of nitrogen obtained by removing oxygen from air. The nitrogen is used to sweep out the capillary tubing before an analysis, thereby displacing gas left in the tubing from a previous analysis. Mercury is used in the slow combustion pipette *c*.

Correction of Analyses for Molecular Volume.

Tables VI., VII., and VIII., containing the results of analyses of Pittsburgh natural gas, methane, and carbon monoxide, will serve to show the magnitude of the errors introduced into the calculation from the combustion data when no account is taken of the true molecular volumes of the gases entering into the reactions.

The values for natural gas are calculated by use of the formulae following. The ordinary equations in which *x* represents partial methane and *y* partial ethane serve to obtain the partial pressures of the constituents closely enough for the authors' purposes. Hence—

$$2x + 2.5y = \text{contraction,}$$

$$x + 2.0y = \text{carbon dioxide produced.}$$

From which *x* and *y* are calculated.

TABLE VIII.—Analyses of Pittsburgh Natural Gas.

Item.	2.16.13.	Sample— 2.1.13.	9.15.12.	12.1.12.
Volume of sample taken, cc.	31'20	31'55	30'70	31'20
Volume after carbon dioxide absorption, cc. . .	31'20	31'55	30'70	31'20
Part taken, cc.	31'20	31'55	30'70	31'20
Oxygen added, cc.	91'90	92'80	95'20	90'15
Total volume, cc.	123'10	124'35	125'90	121'35
Volume after burning, cc. .	58'10	58'60	62'30	56'45
Contraction, cc.	65'00	65'75	63'60	64'90
Volume after carbon dioxide absorption, cc. . . .	21'90	22'00	27'10	20'45
Carbon dioxide	36'20	36'60	35'20	36'00
Methane from theoretical equation, per cent . .	84'4	84'5	85'1	85'1
Ethane from theoretical equation, per cent . .	15'8	15'8	14'8	15'2
Total paraffins from theoretical equation, per cent	100'2	100'3	99'9	100'3
Methane from corrected equation, per cent	83'6	83'7	84'3	84'3
Ethane from corrected equation, per cent	16'3	16'2	15'2	15'7
Total paraffins from corrected equation, per cent	99'9	99'9	99'5	100'0
Difference, total paraffins theoretical minus corrected	0'3	0'4	0'4	0'3

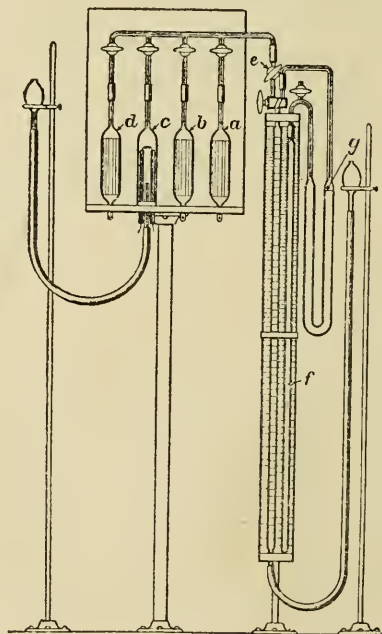


FIG 1.—APPARATUS FOR ANALYSIS OF COMBUSTIBLE GASES.

The partial pressure of the carbon dioxide is obtained in all analyses by dividing the carbon dioxide produced by the combustion by the volume after burning, and multiplying the result by 760.

The corrected equations take the following form for these particular calculations:—

$$2.003x + 2.5y = \text{contraction,}$$

$$0.997x + 2.0y = \text{carbon dioxide produced,}$$

From which *x* and *y* are calculated.

It will be noticed that the molecular volumes of the ethane and of the carbon dioxide produced from it alone have been taken as 1,000, because the partial pressures of the gases are so low that no appreciable error is introduced into the calculation by this procedure. However, if the ethane as shown by the ordinary equations were 25 per cent or higher, as is the case in many natural gases, suitable corrections would have to be made for the molecular volumes of ethane and of carbon dioxide produced by its combustion.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

BANANA ESSENCE.

Chemists who are clever in discovering in plants and fruits the products which give them their delicate perfume, have not yet been able to determine the nature of the aroma of the banana; M. Kléber, by making a large branch of bananas ripen, then by instilling steam into the strong aromatised fruit, previously peeled, has just been able to obtain a few drops of essence having the characteristic odour of the banana. Acetate of amyl forms the basis of the perfume. It is the first time that the presence of an ether of amyl alcohol has been remarked in a natural essence. Up till now it has always been considered that the presence of these ethers, employed in the manufacture of essences and of artificial perfumes, was bad for health. Nature has just shown us that this is not the case. Acetate of amyl is found naturally in the banana, in small amount, it is true, but completely harmless.

MICROBES AND THE SOLAR RAYS.

M. Roux communicates to the Academy a work of Mme. Victor Henri, which opens a road for the applications of ultra-violet rays. By exposing, in a certain way, to the rays of mercury lamp, it is seen that beside the microbes that are killed, a certain number continue to exist, which from the fact of irradiation, undergo a great change. Thus, for example, for the microbes of charbon, new races of microbes can be created, which instead of being formed of long rods are round, are completely distinguished by their reactions, and provoke in the animal a malady of quite a different type to that caused by normal charbon. This result brings up the hypothesis that the very numerous different microbes that are to be found in nature are merely the varieties of a small number of primitive types which have become transformed from the effects of a more or less prolonged action of the sun's light and from the conditions of environment.

A TREATMENT OF CHARBON.

Dr. Roux, Director of the Pasteur Institute, has made an important communication in the names of Messrs. Louis and Charles Fortmean, of Nantes, concerning a treatment of a great malady of charbon, by subcutaneous injections of sterilised cultures of *ptiocyanic bacilli*. These two doctors have treated about 50 patients attacked by charbon, and have only had to register 5 deaths. One single injection generally suffices to cure bacterian charbon. In the rather more serious cases two injections are sufficient.

THE GASES OF THE NEBULÆ.

More than ten years ago, the astrophysicians had discovered in the sun a gas unknown on the earth and to which was given the name of helium. This rare gas was discovered in the atmosphere. A few years ago, the science of spectroscopy discovered in the nebulæ, these worlds in a state of formation, the rays of two gases unknown on our globe; to one of these gases was given the name of *Nebulium*, and its ray is ultra-violet. The other gas has not yet received a name; its ray is green. Three physicists of Marseilles, MM. Bourget, Charles Fabry, and Buisson, have succeeded in determining the

atomic weight of *Nebulium*. *Nebulium* has an atomic weight superior to that of hydrogen and inferior to that of helium. It is about 3; and a remarkable fact is that *Nebulium* finds its place in the classification of rare gases made by Rydberg. MM. Bourget, Fabry, and Buisson have likewise succeeded in determining the temperature of the *Nebula Gion*. It is about 15,000°.

GREEN COAL.

Prof. Labbé, Senator of the department of Orne, has presented a very interesting work of M. Henri Bresson which includes eight hydrographic maps of the Normandy region. By making use of unedited documents of the Agriculture Office, M. Bresson has drawn up the statistic of all the Normandy hydro-electric forces. The green coal of the streams and rivers, so called in opposition to the white coal formed by the torrents and waterfalls of the mountains, can give large quantities of energy. At the present time, in the eight departments of Orne, Rure et Loir, Sarthe, Mayenne, Maine et Loir, Manche, Calvados, and Eure, there are thirty-six hydro-electric installations; but the utilisation of Normandy green coal could be much more considerable.

THREATENED CHANGE IN THE FRENCH METRICAL SYSTEM.

The creation of the French Metrical System, the use of which has become almost universal, is one of the finest victories of which France can boast. In the beginning of this month a Bill on the unities of measure was brought before Parliament, which, if passed, would, according to the opinion of very many men competent on the matter, destroy the definitions that are the fundamental principles of this system. There was some fear that this law might be, as it were, smuggled through and voted surreptitiously, and that is exactly what has happened. On April 3rd, in the heat of the tumult caused by the Rochette affair, the Bill was brought before the House and declared. No one asked to speak over it in the general discussion, and when put to the vote it was at once adopted by the deputies, not one of whom knew what it was about. But the veto still remains for the Senate, who will perhaps be better informed and rather more curious as to what they are asked to vote about.

FLIES AND MOSQUITOES DISLIKE COD LIVER OIL.

A former army veterinary surgeon, M. Lang, has been making some very interesting experiments in Noumea on flies and mosquitoes, gadflies, &c. These experiments have proved that cod liver oil possesses a very pronounced toxic action on these noxious insects. When it is spread over the surface of stagnant water it kills the larva of these flies much more rapidly than schiste oil, and moreover keeps away other winged insects. The evaporation of this oil is very slow, and it has besides no caustic action on the skin, so that if a horse is smeared over with cod liver oil, in a few minutes it is freed from flies that torment it so much, especially when it is afflicted with wounds and sores, the cure of which is often thus favoured and hastened. But, unfortunately, besides the penetrating and particularly disagreeable odour of cod liver oil, its expense will necessarily limit the employment of this new process.

TWO INTERESTING SCIENTIFIC CONGRESSES.

Two interesting scientific Congresses are being held this week in Paris. One is the 5th Congress of Physiopathy, which is being held in the Faculty of Medicine, and presided over by Prof. Maurel, of Toulouse. The subject that is to be especially studied at this Congress is the action of physical agents in gout, in ankylosis, and in lupus. The other Congress is to be held at the Sorbonne, and is the fifty second Congress of the *Société des Savantes* of Paris, and is to be held under the auspices of the Minister of Public Instruction, M. Bienvenu-Martin. In the South of France, on the Azur Coast at Cannes, is also to be held this week the Congress of the International Association of Thalassopathy.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Annual General Meeting, March 26, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President,
in the Chair.

DR. M. O. FORSTER drew attention to an article signed by Prof. H. E. Armstrong, appearing in the *Chemical World* for March, 1914, and asked the President the following question:—

"What action have the Council taken or do they propose taking to defend one of their salaried officials from an imputation of inefficiency uttered in a public journal by a Vice-President who has filled the office of President?"

The PRESIDENT, in reply, stated that the matter had received the earnest attention of the Council, who had passed the following resolution:—

"That the Council of the Chemical Society emphatically repudiates the uncalled-for remarks made by Prof. Armstrong in an article in the March, 1914, number of the *Chemical World* which appear to imply literary incompetence on the part of the Editor of the Society's Publications, and offers to Dr. Cain an expression of its continued confidence in and appreciation of his work as Editor";

and that a copy of this resolution has been sent to Prof. H. E. Armstrong, Dr. J. C. Cain, and also to the Editor of the *Chemical World*, asking him to insert the resolution in a prominent position in the next number of that journal.

Dr. G. D. Lander and Dr. F. L. Pyman were appointed Scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year.

The Report of the Council on the progress of the Society during the past year was presented, and the TREASURER made a statement as to the income and expenditure. The adoption of the Report of Council, together with the Balance Sheet and Statement of Accounts for the year ended December 31, 1913, was proposed by Dr. N. V. SIDGWICK, seconded by Dr. R. H. PICKARD, and carried unanimously.

A vote of thanks to the Auditors was proposed by the TREASURER and acknowledged by Dr. S. RIDEAL.

Report of Council, 1913—1914.

The Council are gratified to be able to report that the membership of the Society has continued to expand during the past year. On December 31, 1912, the number of Fellows was 3158. During 1913, 164 Fellows were elected, and 2 have been reinstated, making a gross total of 3324. The Society has lost 26 Fellows by death, 40 Fellows have resigned, the elections of 7 Fellows and 1 reinstatement have become void, and 49 Fellows have been removed for non-payment of annual subscriptions.

The total number of Fellows therefore on December 31, 1913, was 3201, showing an increase of 43 over that of the preceding year. On comparing these figures with those given in the previous Report of Council, it will be noticed that the number of elections in 1913 has dropped to the average for the previous six years. The resignations received in 1913 are less by 12 than in the previous year, whilst the number of Fellows removed for non-payment of annual subscriptions still continues very high, notwithstanding the latitude allowed by the Council.

The names of the deceased Fellows, with date of election, are:—Gustavus Anthony Abrines (1890); Matthew Algernon Adams (1877); Edward Louis Barret (1869); J. Carter Bell (1865); William Popplewell Bloxam (1883); Angelo Cantin (1900); Arthur Crozier Claudet (1902); Tom Crossman (1895); James Tudor Cundall (1887); Joseph Davidson (1876); Leopold Mandeville Deane (1886); Frank Standish Findon (1905); Leonard

Clifford Green (1908); Sir Walter Noel Hartley (1866); John Heron (1876); John Hunter (1883); Julius Lewkowitsch (1883); Hugh Marshall (1890); George Matthey (1870); Isaac Patchett (1870); Thomas Ebenezer Pye (1906); Mathura Goolab Roy (1900); Christer Peter Sandberg (1870); Walter Shelley Spencer (1887); William Tate (1890); Arthur Wallace (1912).

The number of Honorary and Foreign Members at the end of 1912 was 33. During 1913, Prof. D. P. Kononovoff and Prof. Alfred Werner were elected; the total number of Honorary and Foreign Members at the present time therefore is 35.

In accordance with the announcement made in the Annual Report presented in March of last year, the following Report deals with the work of the Society during the period between that date and the present Annual General Meeting.

The Council offers its hearty congratulations to Prof. George Downing Liveing (elected November 21, 1853) who has completed over sixty years of Fellowship, and to the following, who have reached their Jubilee:—Mr. William Spiller, elected January 15, 1863; John Whitfield, elected November 5, 1863; Prof. John Wrightson, elected February 4, 1864; Mr. Henry Bassett, elected February 18, 1864.

During the year, 355 scientific communications were made to the Society; 253 of these have been published already in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

The volume of *Transactions* for 1913 contains 2296 pages, of which 2173 are occupied by 238 memoirs, the remaining 123 pages being devoted to the Obituary Notices, the Ladenburg and Van't Hoff Memorial Lectures, the Report of the International Committee on Atomic Weights, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contained 266 memoirs occupying 2431 pages.

The *Journal* for 1913 contains 5978 abstracts, which extend to 2520 pages, whilst the abstracts for 1912 numbered 5497, and occupied 2264 pages.

In accordance with an announcement made at the last Annual General Meeting, a change has been made in the arrangement of the abstracts, those of Physiological Chemistry and the Chemistry of Vegetable Physiology and Agriculture being included in Part I. instead of in Part II., as heretofore. This has led to approximate equality in the size of the two parts.

	No. of pp. in 1913.	No. of pp. in 1912.
Part I.	1432	1044
Part II. (with indexes) . .	1528	1614

The abstracts may be classified as follows:—

PART I.	Pages.		No. of Abstracts.
Organic Chemistry			1824
Physiological Chemistry			771
Chemistry of Vegetable Physiology and Agriculture			442
	1432		3037
PART II.			
General and Physical Chemistry . .			1401
Inorganic Chemistry			555
Mineralogical Chemistry			159
Analytical Chemistry			826
	1088		2941
Total in Parts I. and II. . .	2520		5978

Following the proposal made by the Deutsche Physikalische Gesellschaft, the Council have decided to request authors to insert either their University, Laboratory, or private address at the end of all papers appearing in the *Transactions*. It is hoped that by this means com-

communication between authors of papers in various journals will be facilitated.

During the past year, advantages have been offered to Fellows of the Society by the reduction in price of certain publications. Arrangements have been made by which Fellows can obtain Vol. I. of the "Literatur Register," by R. Stelzner, at the reduced price of £3 10s. (original price, £4 4s.), provided that not less than twenty copies of the work be purchased by Fellows. Application for this volume should be addressed to the Honorary Secretaries. Fellows will also be able to purchase the forthcoming Vol. III. of the "International Tables of Physical Constants and Numerical Data at the reduced price of 19s. 3d. (unbound), or £1 2s. 3d. (bound).

Vol. V. of the "Collective Index" of the *Journal and Proceedings of the Chemical Society* (1903—1912) has been issued during the year, Part I. ("Author Index") appearing in May and Part II. ("Subject Index") in December. The price of this volume is now £2 to Fellows and £2 10s. to the public.

The Council have decided to offer the Jubilee Volume (giving a history of the Society from 1841 to 1891), which was published at 6s., at the reduced price of 2s. 6d., and also to dispose of a few bound sets of the *Journal of the Chemical Society*, from 1871 to 1900 inclusive (published at £47 10s.), at £20 for the series.

The attention of Fellows is directed to the appearance of a French translation of Vol. IX. of the "Annual Reports." Permission was granted to the Director of the Laboratoire Municipal de Paris for the production of this translation; it was published by Messrs. Hermann et Fils in October last at the price of fr. 7.50.

An intimation has been received from the Faraday Society that this body is prepared to consider the election to membership of a certain number of Fellows of the Chemical Society without payment of an entrance fee.

The *Transactions* for 1913 contain obituary notices of Paul Emile Lecoq de Boisbaudran, Edward Divers, Humphrey Owen Jones, John William Mallet, Henry de Moenthal, Benjamin Edward Reina Newlands, John Pattinson, Arthur Richardson, John Wade, and William Ord Wootton, who died during 1912, and the Council desire to express their indebtedness to the Fellows who wrote these notices.

The Council also wish to record their thanks to those Fellows who contributed to Vol. X. of the "Annual Reports."

During the past year, the Society has been privileged to listen to Memorial Lectures on Jacobus Henricus van't Hoff, delivered by Prof. James Walker, and Albert Ladenburg, delivered by Prof. F. Stanley Kipping. In the last Report of Council it was stated that when these two lectures had been delivered the Council would publish Vol. II. of the "Memorial Lectures." This volume has now been issued (price 6s.), and can be obtained from the publishers or from the Assistant Secretary.

The Council have under consideration the desirability of re-issuing Vol. I. of the "Memorial Lectures" (now out of print). To assist them in arriving at a decision in the matter, a circular was issued with *Proceedings* No. 423 inviting those Fellows who would be willing to purchase Vol. I. (price, 10s. 6d.) to notify the Assistant Secretary.

The Council are pleased to announce that the Faraday Lecture is to be delivered by Prof. Svante August Arrhenius, F.R.S., on Monday, May 25, 1914, at 6 p.m., in the Theatre of the Royal Institution (by the courtesy of the Managers). The title of the lecture is "Electrolytic Dissociation."

To meet the convenience of Fellows, the Council decided that a list of the papers to be read at each Ordinary Scientific Meeting of the Society should be advertised in the *Morning Post* on the Wednesday previous to the day of meeting. This list of papers appears on the front page, at the top of the extreme right-hand column.

The stock of apparatus and reagents for the use of

Fellows making experiments at the meetings of the Society has been replenished. A list of such apparatus and reagents can be obtained from the Assistant Secretary.

In order to afford Fellows an opportunity of meeting informally, the rooms of the Society were open on the evening of January 15, 1914, when the President and Council were present to receive the Fellows. The Council have decided to provide for a similar meeting on Thursday, April 30, from 8 to 10 p.m.

The Anniversary Dinner of the Society was held at the Whitehall Rooms, Hôtel Métropole, on March 14, 1913, Professor Percy F. Frankland, the retiring President, occupying the Chair. An abbreviated account of the speeches made, together with a list of the names of the Fellows and their guests who were present, appears in the *Proceedings*.

It is with very great pleasure that the Council have to report that a bust of the Right Honourable Sir Henry Enfield Roscoe, by Mr. Alfred Drury, R.A., has been presented to the Society by the friends and former students of Sir Henry Roscoe. The presentation was made before a distinguished company in the Rooms of the Society on November 20, and the bust now adorns the Library.

The meeting of the International Association of Chemical Societies was held in Brussels instead of in London, as previously arranged, in September, the Society being represented by Sir William Ramsay, K.C.B., Prof. Percy F. Frankland, and Prof. Arthur W. Crossley. An abbreviated report of the meeting appears in the *Proceedings*. Thanks to the generosity of M. Ernest Solvay, the Association is now endowed with a sum of Frs. 250,000, in addition to a yearly income of Frs. 37,500 for twenty-eight years, and a site for offices in Brussels.

To celebrate the centenary of the birth of Sir John Bennett Lawes in 1814, and of Sir Henry Gilbert in 1817, it is proposed to erect a Commemoration Laboratory at Rothamsted. Fellows have been invited to respond to the appeal which is being made to raise £6000, this being half the total amount required for the memorial, the other half having been promised in the form of a grant.

Mention was made in the last Report of Council that the sum of £65 4s. had been subscribed by the Fellows of the Chemical Society towards the van't Hoff Memorial. In April, 1913, the total sum of Fl. 51,000 had been received by the Committee, and a statement with reference to the disposal of this fund is given in the *Proceedings*.

The Council have decided to make a further contribution of £10 to assist the International Commission to prepare the fourth volume of the International Tables of Constants and Numerical Data.

The number of books borrowed from the Library during the year 1913 was 1730, as against 1825 the previous year; of these, 546 were issued by post, as against 491 in the preceding year.

The Additions to the Library comprise: 137 books, of which 68 were presented, 510 volumes of periodicals (representing 241 journals), and 86 pamphlets, as against 135 books, 482 volumes of periodicals (representing 237 journals), and 76 pamphlets last year.

The question of providing for the continuous growth of the Library has been further considered, and a room in the basement has been altered to accommodate 27 rolling book-stacks, estimated to contain 8500 volumes, or twelve years' addition to the Library at its present rate of growth.

From a purely financial point of view, the past year was not so successful as the year immediately preceding it. Notwithstanding the considerable cost of the redecoration and the improvements in the ventilation of the Society's Rooms, there was a balance in 1912 of £176 1s. 7d., whilst in 1913 there is a deficit of £237 7s. 7d. on the year's working. A careful examination of the statement of income and expenditure, however, will show that this need cause no alarm. From all sources, the income for 1913 amounts to £9235 14s. 1d., as against £8120 12s. 3d. in 1912, an increase of £1115 1s. 10d., whilst the corre-

sponding expenditures are £9473 1s. 8d. and £7944 10s. 8d., an increase of £1528 11s. The income, as well as the expenditure, is a record one, and the amount of each has been raised by a common cause. The printing of Volume V. of the Decennial Index alone has added £1378 to the normal expenditure, whilst somewhat over £1000 has already been added to income from its sale. Remembering that Part II. (Subject Index) was only published in December last, it may confidently be anticipated that sales of this volume in the near future may very considerably reduce, if not altogether obliterate, the deficit arising from this source.

Another exceptional expenditure which could not be delayed was the provision of new iron bookcases for the extension of the Library in one of the basement rooms at a cost of £155 13s. The extra cost of the *Journal* this year was due to the increase of about £63 in Abstractors' fees, and a consequent increase of equal amount in the cost of printing. The cost of the Annual Reports on The Progress of Chemistry for 1912 exceeded that for 1911 by £51. It is to be regretted that the amounts received as Life Compositions and Admission Fees were £141 less than in 1912, when they were, however, considerably above the average.

In the balance-sheet a sum of £168 1s. 10d. appears as an asset, having been paid on account of the International Association of Chemical Societies. This temporary expenditure is owing to the meeting of the Association having been originally arranged to take place in London, but it will shortly be repaid to the Society from the Fund endowed by M. Ernest Solvay to which reference has already been made.

The net income of the Research Fund from investments is about £343, and to this was added £77 16s. 3d., being unexpended grants from previous years which were returned. From this, grants amounting in all to £368 were made, leaving £50 to be added to the balance in hand.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year was proposed by Dr. BERNARD DYER, seconded by Dr. L. T. THORNE, and acknowledged by Sir WILLIAM RAMSAY.

The PRESIDENT then delivered his Address, entitled "Tautomerism." A vote of thanks to the President, coupled with the request that he would allow his Address to be printed in the *Transactions*, was proposed by Prof. R. MELDOLA, seconded by Prof. W. JACKSON POPE, and carried with acclamation, the PRESIDENT making acknowledgment.

The Report of the Scrutators was presented, and the President declared that the following had been elected as Officers and Council for the ensuing year:—

President—W. H. PERKIN, Sc.D., LL.D., F.R.S.

Vice-Presidents who have filled the office of President—Henry Edward Armstrong, Ph.D., LL.D., F.R.S.; Alexander Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, O.M., D.Sc., P.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; Harold Bailey Dixon, M.A., Ph.D., F.R.S.; Percy Faraday Frankland, Ph.D., LL.D., F.R.S.; Augustus George Vernon Harcourt, M.A., D.C.L., F.R.S.; Raphael Meldola, D.Sc., LL.D., F.R.S.; Hugo Müller, Ph.D., LL.D., F.R.S.; William Odling, M.A., M.B., F.R.S.; Sir William Ramsay, K.C.B., LL.D., F.R.S.; James Emerson Reynolds, Sc.D., M.D., F.R.S.; the Rt. Hon. Sir Henry Enfield Roscoe, LL.D., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William Augustus Tilden, D.Sc., F.R.S.

Vice-Presidents—Herbert Brereton Baker, M.A., D.Sc., F.R.S.; Peter Phillips Bedson, M.A., D.Sc.; Horace Tabberer Brown, LL.D., F.R.S.; Charles Thomas Heycock, M.A., F.R.S.; Edmund James Mills, D.Sc., LL.D., F.R.S.; Gilbert Thomas Morgan, D.Sc.

Treasurer—Alexander Scott, M.A., D.Sc., F.R.S.

Secretaries—Samuel Smiles, D.Sc.; James Charles Philip, M.A., D.Sc., Ph.D.

Foreign Secretary—Arthur William Crossley, D.Sc., Ph.D., F.R.S.

Ordinary Members of Council—George Barger, M.A., D.Sc.; the Rt. Hon. the Earl of Berkeley, F.R.S.; Edward John Bevan; Adrian John Brown, M.Sc., F.R.S.; Harold Govett Colman, D.Sc., Ph.D.; Arthur Harden, D.Sc., Ph.D., F.R.S.; Thomas Martin Lowry, D.Sc.; Kennedy Joseph Previté Orton, M.A., Ph.D.; Robert Henry Aders Plimmer, D.Sc.; Edward John Russell, D.Sc.; George Senter, D.Sc.; John Millar Thomson, LL.D., F.R.S.

PHYSICAL SOCIETY.

Ordinary Meeting, March 27, 1914.

Prof. Sir J. J. THOMSON, O.M., F.R.S., President, in the Chair.

A PAPER ON "A New Type of Thermogalvanometer" was read by Mr. F. W. JORDAN.

The puff of air from an orifice in an air chamber when the air within is suddenly heated is utilised in this instrument to deflect a small suspended vane. The current to be measured is made or broken through a heater of small thermal capacity in the air chamber and the outrush or inrush of air through the orifice delivers an impulse to the vane. The disturbing effects of extraneous heat and pulsations of external pressure are eliminated by a compensation method. In one instrument of this type the sensibility was 4 mm. per microwatt and the extremity of the throw of the vane was attained in two seconds.

DISCUSSION.

Dr. W. H. ECCLES said a good deal of work had been done with convection galvanometers, but Mr. Jordan was the first to measure the pulses produced by suddenly heated filaments. About nine years ago he had made some small instruments consisting of a fine filament connected to heavier leads and mounted in a small glass tube suitable for insertion in the ear. If an interrupted current passed through the filament the observer could hear every pulse produced. The instruments varied in sensitiveness. One which had a platinum filament of 12 ohms resistance could detect 0.0025 ampère, while another, with a platinised quartz filament of 900 ohms, could detect 0.00003 ampère.

Mr. W. DUDELL thought the instrument was very ingenious. He asked if the sensitiveness could be increased to measure quantities of energy of the order of a microwatt.

Mr. JORDAN, in reply, stated that the fibre was already extremely fine as the inertia was small. He thought the vane could be reduced considerably and the sensitiveness thereby increased without a serious increase in the time of swing.

A paper describing "An Instrument for Recording Pressure Variations due to Explosions in Tubes" was read by Mr. J. D. MORGAN.

The object of this paper is to describe a mechanical oscillograph for recording the pressure variations which accompany a gas or other explosion in an open tube.

A light steel vane of rectangular form is employed and this is mounted parallel to the explosion tube in a cell presenting a lateral opening to the tube interior. Along three edges the vane is free, and along the fourth edge it is attached to a torsion wire. The vane is made to fit the cell as closely as possible around its edges without touching the sides of the cell. The diagram is produced by a style on a smoked paper strip wrapped around a clock driven drum, and on the same strip is described a time curve by an electrically-driven tuning fork of known frequency.

To make the instrument dead beat a dash-pot is mounted on the front of the vane cell and attached to the style.

DISCUSSION.

The CHAIRMAN asked if the author thought all the phenomena shown in some of his curves were features of the original explosion, or if some of them were due to reflected disturbances from the walls and ends of the tube.

Mr. R. APPLEYARD said the different types of curve shown by the author seemed analogous to the oscillatory and aperiodic types of electric discharge. He asked if the author had tried damping with a magnet and copper plate.

Dr. W. WATSON expressed his interest in the instrument. He mentioned with reference to the statement that a diaphragm cannot be made to give a uniform scale, that with a corrugated diaphragm a quite uniform scale of displacement against pressure could be obtained. He believed the author found it advantageous to have considerable inertia in the moving system, and he thought the inertia would play an even more important rôle in defining the extent of the vane's motion under the influence of a sudden expansion than the torsional control. He thought that the effect on the resultant curves of varying the inertia ought to be investigated. He supposed that in the curves shown the disturbance was compounded of what he might call the organ-pipe effect, and another effect due to the time taken by the combustion wave to pass along the tube.

The AUTHOR, in reply, said he had considered electro-magnetic damping, but rejected it on account of relative cost. There were, however, grave objections to the use of the dash-pot, which undoubtedly modified the shape of the curves. There was no doubt that the resultant disturbances were compounded of a pressure wave along the tube and a surging of the gas as a whole. It was difficult to separate the effects. In most cases—probably in all—the flame seemed to last as long as the needle was vibrating.

A paper entitled "*The Direct Measurement of the Napierian Base*," was read by Mr. R. APPLEYARD.

The author described a simple apparatus intended to convey to students an idea of the way in which the base e of the Napierian logarithms enters into physical problems in a specific case of wide application. A small length of chain is allowed to hang from a loop of thread, and the remaining part of the chain is then pulled aside until the thread is at 45° to the vertical. The curved portion becomes a true catenary when the angle between the vertical and curved portions of chain at the attachment of the loop is 90° . To ensure that this condition is reached, the circle of curvature of the catenary at that point is drawn, and this is found to have a radius equal to the vertical portion. In these circumstances, if the vertical length is taken as unity, and if its lower end is taken as origin, it is shown that e is the sum of the y -ordinate at $x = 1$, and the length of curved chain between the point where that y ordinate cuts the curve and the top of the vertical portion. The application of this result to a simple representation of the relationship and meaning of hyperbolic functions was also shown, and it was urged that such functions should be studied from consideration of the catenary rather than from the hyperbola.

DISCUSSION.

The CHAIRMAN supposed the object of the paper was to familiarise students with the properties of the catenary rather than the determination of e , as this was so easily obtained from the formula.

Dr. W. H. ECCLES drew attention to a method of measuring e from the properties of the catenary, which the late Prof. Minchin used to set as a practical problem in the London University examinations.

NOTICES OF BOOKS.

Chemistry and its Borderland. By ALFRED W. STEWART, D.Sc. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

THIS book gives a very interesting account of some recent developments of chemistry, such as can readily be followed by the general reader who is not altogether ignorant of the elements of the science. The relations of chemistry, firstly to the other sciences and then to the industries, are treated in the first chapters, and then recent advances in some special branches which have developed more or less independently are admirably summarised. Thus a chapter is devoted to immuno-chemistry and another to spectroscopic work. Radio-activity and the nature and the transmutation of the elements are considered at some length, and the last chapters are given to the discussion of some chemical problems of the present and the future and to the methods and organisation of chemical research. These later chapters contain some excellent suggestions for schemes for training research chemists, and throughout the book great stress is laid upon the practical and commercial value of pure research. The author writes in a style which is neither too technical nor too elementary, and he is particularly happy in his choice of illustrations and analogies to explain some rather difficult conceptions.

The Co operation of Science and Industry. By S. ROY ILLINGWORTH, A.R.C.Sc., A.I.C., B.Sc.(Lond.). London: Charles Griffin and Co., Ltd. 1914.

THIS little book, for which Sir Boverton Redwood has provided a fore-word, has been written for business men, with the special aim of pointing out to them the help from a genuine commercial point of view which science can give the Industries. There is certainly need for bringing before the commercial world and the general public the advantages of the co-operation of science and industry, and the author writes clearly and convincingly on the subject. He discusses at some length the problem of the training of scientific and business men, and gives an outline of the excellent scheme of education which has been adopted in Austria. In concluding he shows how the increasing keenness of competition in every branch of commerce must be met by increased efficiency of business men, and points out how essential it is to the welfare of the nation that industry and science should work together hand in hand.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 9, March 2, 1914.

Polymorphism of Camphor.—Fred Wallerant. — When camphor is allowed to crystallise after fusion it is found to be at least quadrimorphic. It is first seen to form cubic crystals, which are transformed as the temperature decreases into rhombohedral crystals, the temperature of transformation being 97° . The ternary crystals are not identical with those obtained by the crystallisation of an alcoholic solution. If one of these large crystals is observed it is noticed that small crystals strongly resembling the primitive crystals form on its edges. The rate of transformation is very small and increases as the temperature is raised. The new crystals are the stable form, for the inverse transformation never takes place. The rhombohedral crystals when cooled to -28° are transformed into new rhombohedral crystals.

Ether-oxides of Carvacrol.—Paul Sabatier and A. Mailhe.—When a mixture of vapours of carvacrol and methanol are passed over oxide of thorium at $420-450^\circ$,

a yellow fluorescent liquid is obtained. On fractional distillation this yields a certain amount of mixed oxide of carvacryl and methyl, while the portion passing over above 300° contains oxide of carvacryl. If the catalytic dehydration occurs at a higher temperature prismatic crystals of oxide of dicarvacrylene may be obtained from the resulting liquid. From carvacrol and ethanol small quantities of the mixed oxide of ethyl and carvacryl can be obtained. With carvacrol and phenol mixed oxide of carvacryl and phenyl is obtained, and also oxides of carvacryl and dicarvacrylene.

New Method of Preparing Tricarballic Acid.—H. Gault.—When oxalocitric lactone is heated to 130–150° at the ordinary pressure carbon dioxide is evolved and a liquid is obtained, which on saponification with dilute mineral acids gives crystallised tricarballic acid quantitatively. The total yield is about 45 per cent calculated from the oxalacetic ether distilled. If, however, it is referred to the original oxalic ether the yield is only 20 per cent.

Vol. clviii., No. 10, March 9, 1914.

Reduction of Nickel Protoxide and Existence of Suboxide of Nickel.—Paul Sabatier and Léo Espil.—The authors have studied quantitatively the reduction of nickel protoxide by hydrogen, determining not the loss of weight but the weight of water formed. They find that the oxide is reduced more slowly the higher the temperature at which it has been prepared. The reduction is practically proportional to the velocity of the current of hydrogen, and the rate of reduction is an exponential function of the temperature. The progress of the reduction indicates the existence of a suboxide which is slowly reduced by hydrogen at the same temperatures as the protoxide, the final product being free nickel. The presence of water-vapour in the hydrogen diminishes the velocity of reduction.

Determination of Contested Atomic Weights by the Application of the Laws of Transparence of Matter to X-rays.—Louis Benoist and Hippolyte Copaux.—Since transparence towards the X-rays is an intrinsic property of the atom the determination of the equivalent of transparence of an element enables a position on the curve of isotransparence to be assigned to the element, the atomic weight of which is thus fixed. This method of finding atomic weights has the advantage of being entirely independent of any conditions which might make the physico-chemical properties vary. When applied in the case of thorium it shows that the atomic weight is 232, while that of cerium is 140.25.

Preparation of Acetylenic Glycols from their Dimethyl Ethers.—R. Lespieau.—Chloromethylic ether reacts with the acetylenic magnesium derivatives to give ether oxides. In order to demethylate these oxides it is first necessary to fix two atoms of bromine at the double bond, and then subject them for some hours to a current of hydrobromic acid at 100°. The acetins are then obtained by the action of silver acetate, and then saponification gives the brominated glycols. Finally, the bromine is removed by means of zinc powder and alcohol. Thus from $\text{CH}_3\text{OCH}_2\text{C}\equiv\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}\equiv\text{C}\cdot\text{CH}_2\cdot\text{OCH}_3$ the new glycol $\text{CH}_2\text{OH}\cdot\text{C}\equiv\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}\equiv\text{C}\cdot\text{CH}_2\cdot\text{OH}$ can be obtained.

Stereo-chemical Isomers of some γ -Glycols.—Georges Dupont.—Of the two stereochemical isomers into which it is possible to separate acetylenic γ -glycols one should be separable into optical inverses. Generally speaking one is much less soluble in most solvents than the other, and melts about 30° higher. The author has studied the two glycols sym. di-*p*-tolylbutine diol and sym. di-*p*-methoxyphenylbutine diol in order to determine which isomer is which. His experiments have not led to the desired result, but they show that the isomer which is the easiest to obtain is the one which is most likely to prove separable.

Cyclisation of 1.4-Diketones.—E. E. Blaise.—Di-propionylethane can readily be transformed by the action of methyl alcoholic potash into methylethylcyclopentenone, the yield being about 80 per cent. It seems probable that this method of cyclisation is applicable to all acyclic 1.4 non-methylated ketones, the first member of the series acetylacetone being an exception, for no trace of methylcyclopentenone can be obtained from it.

MISCELLANEOUS.

The firm of Messrs. R. and J. Beck, Ltd., of 68, Cornhill, London, has just produced a binocular microscope which is stated to possess every advantage of a monocular while giving the microscopist the benefit of the stereoscopic relief and comfort of working with two eyes instead of one. It can be instantly converted into a monocular by moving the prism, and judging from the descriptions and illustrations it represents a decided advance in design and efficiency.

MEETINGS FOR THE WEEK.

- MONDAY, 27th.—Royal Society of Arts, 8. (Cantor Lecture). "Some Recent Developments in the Ceramic Industry," by W. Burton, M.A.
- TUESDAY, 28th.—Royal Institution, 3. "Problems of Physical Chemistry," by W. Wahl, Ph.D.
- Royal Society of Arts, 4.30. "The Administration of Imperial Telegraphs," by Charles Bright.
- WEDNESDAY, 29th.—Royal Society of Arts, 8. "The Need for a Better Organisation of Economic and Industrial Resources," by C. R. Enock.
- THURSDAY, 30th.—Royal Institution, 3. "The Last Chapter of Greek Philosophy—Plotinus as Philosopher, Religious Teacher, and Mystic," by The Very Rev. W. R. Inge, D.D.
- Royal Society. "Lack of Adaptation in the Tristi-chacæ and Podostemacæ," by J. C. Willis.
- "Genetics of Tetraploid Plants in *Primula sinensis*," by R. P. Gregory. "Action of certain Drugs on the Isolated Human Uterus," by J. A. Gunn. "Presence of Inorganic Iron Compounds in the Chloroplasts of the Green Cells of Plants considered in Relationship to Natural Photosynthesis and the Origin of Life," by B. Moore. "Influence of Osmotic Pressure upon the Regeneration of *Gunda ulvæ*," by D. J. Lloyd.
- "*Glossina brevipalpis* as a carrier of Trypanosome Disease in Nyasaland" and "Trypanosome Diseases of Domestic Animals in Nyasaland, *Trypanosoma procurrens*—Part III., Development in *Glossina morsitans*," by Surg.-Gen. Sir D. Bruce, Major A. E. Hamerton, Capt. D. P. Watson, and Lady Bruce.
- FRIDAY, May 1st.—Royal Institution, 9. "A Criticism of Critics," by E. F. Benson, B.A.
- Royal Institution, 5. Annual Meeting.
- SATURDAY, 2nd.—Royal Institution, 3. "Similarity of Motion in Fluids," by T. E. Stanton, D.Sc., &c.

ERRATUM.—P. 182, col. 2, line 1, for "ought to be laid" read "ought not to be laid."

INSTITUTE of CHEMISTRY OF GREAT BRITAIN AND IRELAND.

Founded 1877. Incorporated by Royal Charter 1885.

The next INTERMEDIATE EXAMINATION will commence on TUESDAY, JUNE 30, 1914. FINAL EXAMINATIONS will commence on MONDAY, JUNE 29, or JULY 6.

The ENTRY LIST will be CLOSED on MAY 26. Forms of application and further particulars can be obtained from the REGISTRAR, Institute of Chemistry, 30, Bloomsbury Square, London, W.C.

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A Register of Fellows and Associates of the Institute of Chemistry who are seeking appointments is kept at the Offices of the Institute. Applications for the services of Professional Chemists should be forwarded to the Registrar.

THE CHEMICAL NEWS

VOL. CIX., No. 2840.

NOTE ON THE DETECTION AND ESTIMATION OF HYDROXYLAMINE.

By HAROLD SCHROEDER.

ANGELA (*Gazzetta*, 1893, xxiii., [2], 102) describes a test for hydroxylamine, employing caustic soda and sodium nitro-prusside.

The author found that the somewhat meagre manipulative details given in the above paper were not sufficiently precise to make the test of value in case of a negative result.

It was found as the result of experiment that, by slight modifications in the manipulation, Angeli's test could be rendered rapid and reliable, and could, moreover, be successfully applied to quantitative estimations.

The test liquid is carefully neutralised, using hydrochloric acid and caustic soda. Two cc. of the liquid are then measured into a 5 in. by $\frac{3}{8}$ in. test-tube, 1 mgrm. of solid sodium nitro-prusside added, and the whole made alkaline with 1 cc. of N/10 caustic soda. The tube is then shaken and rapidly brought up to 100° C. in a water-bath.

It is advisable to keep fairly close to the above proportions.

In the presence of hydroxylamine at a concentration of 0.01 per cent a characteristic magenta colour develops, as stated by Angeli.

The magenta colour lends itself over to colorimetry, and it is easily possible to estimate small amounts of hydroxylamine by comparing the colour of the test liquid diluted to 50 cc. in a Nessler glass with the colour due to a known amount of hydroxylamine.

The colour can also be matched by a mixture of methyl-orange and phenolphthalein, and a set of standards made once for all. The method has been used by Mumford (*Proc. Chem. Soc.*, 1914).

Frankland Laboratory, University of Manchester.

SIMPLE AND COMPLEX ROTATORY DISPERSION.*

By T. MARTIN LOWRY and T. W. DICKSON.

(Concluded from p. 189).

C. Anomalous Rotatory Dispersion in Ethyl Tartrate.

THE following data are taken from an early series of observations on ethyl tartrate, but have not been published previously. The rotations shown are the actual readings for a Cdm Column of the tartrate at 20° C. A much more detailed examination of the form of the dispersion curves for this ester is in progress, but the figures now put forward are sufficiently exact to show that these more complex curves can be represented by a Drude formula containing two terms of opposite sign. The photographic data are taken from some of the earliest observations made by this method and have no claim to be exact; but they have the merit of showing that, as the limit of the visible spectrum is approached, the rotation changes in sign and the ester becomes strongly lævo-rotatory (the lævo-rotation has been traced since as far as -83°); moreover, the curve, as thus greatly extended, adheres closely to the course marked out for it by measure-

ments made in the region in which visual observations can be taken.

TABLE I.—Anomalous Rotatory Dispersion in Ethyl Tartrate.

$$\delta = \frac{132.78}{\lambda^2 - 0.026} - \frac{103.05}{\lambda^2 - 0.061}$$

		Observed.	Calculated.	Calc.-Obs.
Cd red ..	6708	50.06°	50.26°	+0.20
Zn red ..	6364	51.03	50.78	-0.25
Na yellow	5893	53.32	53.32	±
Cu yellow	5782	53.60	53.63	+0.03
Hg yellow	5780	53.69	53.63	-0.06
Cu yellow	5700	53.58	53.74	+0.16
Hg green	5461	53.42	53.36	-0.06
Cu green	5219	51.49	51.41	-0.08
Cu green	5154	50.62	50.50	-0.12
Cu green	5105	49.53	49.72	+0.19
Cd green	5086	49.44	49.35	-0.09
Cd blue ..	4678	35.64	35.69	+0.05
Hg violet	4359	10.79	10.76	-0.03

Photographic observations :—

4737	40	39	-1
4413	20	19	-1
4250	0	-3	-3
4133	-20	-22	-2
4034	-40	-42	-2

It should be noticed that the formula given above can be interpreted in a variety of ways. The two free periods are both beyond the limits of observation, and the anomaly is therefore not due to Cotton's phenomenon. But the form which the equation takes might be due to two vibrations of unequal period and opposite activity, as suggested by R. W. Wood; to the superposition of two "partial-rotations," as investigated by Tschugaeff in the case of menthyl camphor-β-sulphonate; or to the actual presence of two distinct substances, as in the mixtures of turpentine and camphor, which were shown by Biot to give rise to anomalous rotatory dispersion.

D. Dynamic Isomerism as a Cause of Anomalous Rotatory Dispersion.

Whilst there is no reason to doubt that anomalous rotatory dispersion (especially in compounds containing several asymmetric carbon atoms) may be due to the superposition of partial rotations of opposite sign, there is good reason to think that this phenomenon is more commonly produced by the presence of two or more different compounds in a liquid which nominally contains only one optically-active constituent. This view was expressed by Arrdtsen in 1858, as a means of interpreting his own observations on the anomalous rotatory dispersion in tartaric acid. After quoting Biot's experiments on the anomalous rotatory dispersion in mixtures of turpentine and camphor, he writes:—

"One then might regard tartaric acid as a mixture of two substances differing only as regards their optical properties, of which one had a negative rotatory power, the other a positive rotatory power, these rotations varying in different proportions with the refrangibility of the light" (*Ann. Chim. Phys.*, 1858, liv., 421).

Two modifications of a substance, differing in their optical properties but identical in chemical behaviour, may be produced—

- By association with the solvent;
- By polymerisation of the solute; or
- By isomeric change.

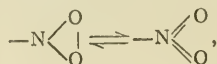
In order that the chemical properties of the two modifications may be the same, it is necessary that these changes should be reversible; if this condition is not fulfilled, the two modifications could indeed be separated by ordinary

* A Contribution to a General Discussion on "Optical Rotatory Power," held before the Faraday Society, March 27, 1914

methods of fractionation, and the liquid would differ in no essential point from Biot's artificial mixtures of dextro- and lævo-rotatory compounds.

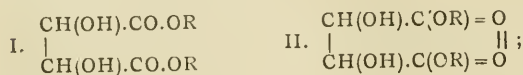
The way in which a homogeneous solid may give rise to a mixture on fusion or dissolution may be illustrated most readily in the case of the reversible isomeric changes, which have been very fully studied under the name of *dynamic isomerism*. It has been shown, for instance, that nitro-camphor changes over in solution (to the extent of about one-sixth) into an acidic isomeride, of opposite rotatory power and probably of unequal dispersive power, thus giving rise to just the right conditions for anomalous rotatory dispersion. The anomaly would here be due to a chemical change belonging to type (iii.), *reversible isomeric change*. All the phenomena would be the same if one of the modifications existed, e.g., in a bimolecular form as $[\text{C}_{10}\text{H}_{15}\text{NO}_3]_2$, but the anomaly would then be attributed to (ii.) *reversible polymeric change*. (The acidic form of nitrocamphor might be expected to polymerise in nonionising solvents, compare acetic in benzene $[\text{C}_2\text{H}_4\text{O}_2]_2$). Further, one of the modifications might combine with the solvent (there is good reason for thinking that normal nitrocamphor forms unstable compounds when dissolved in benzene and its homologues); in this case the phenomena would be precisely similar, but the anomaly might be classified as due to a change of type (i.) *association with the solvent*.

In the case of nitrocamphor, isomeric change in solution is sufficiently slow to give rise to the phenomenon of *mutarotation*, and it was by observations of this kind that this change was first detected. But it is to be expected that anomalous rotatory dispersion may reveal many reversible changes which reach a condition of equilibrium too quickly to be detected or studied by dynamic methods. In the discussion on Pickard and Kenyon's paper (*Proc. Chem. Soc.*, Nov. 20, 1913), it was suggested by one of us (F. M. L.) that a change of type such as that involved in the conversion of trivalent into pentavalent nitrogen—

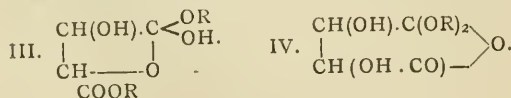


might be demonstrated by observations of anomalous rotatory dispersion in an optically-active nitro-compound, even if too elusive to be detected by any other method. So also an elusive polymerisation may reveal itself by producing anomalous rotatory dispersion in an active liquid, just as the polymerisation of nitrogen dioxide $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ manifests itself in the varying colour of the gas or liquid, although the changes are too rapid to admit of the separation of the two components by ordinary methods.

In the special case of the tartrates, Armstrong and Walker (*Proc. Roy. Soc.*, 1913, A. lxxxviii., p. 399) have suggested four formulae for the isodynamic forms of the acid. In the tartaric esters, two of these modifications might appear as dynamic isomerides—



but the third would probably decompose into an alcohol and an acid-ester, whilst the fourth would be a stable isomeride, not readily convertible into the other forms—



As a matter of fact, ethyl tartrate appears to be a commonplace mixture which can be fractionated by ordinary methods into portions which differ widely in their rotatory power for violet light; it may therefore contain the fixed

ester IV. in addition to various labile forms of the ester I. But methyl tartrate, which is a well-defined crystalline compound and resists fractionation, also shows anomalous dispersion; this cannot be attributed to ordinary static isomerism, but may be due to a dynamic isomerism of one of the more elusive types, in which the change of structure is too rapid to manifest itself by mutarotation in the freshly-prepared solutions. Some such labile isomerism, involving little more than a rearrangement of residual affinities, must also be postulated to account for the anomalous rotatory dispersion in the simple esters described by Pickard and Kenyon. Even more emphatically are the coarser types of isomerism ruled out in the case of naphthylmethylcarbinol, $\text{C}_{10}\text{H}_7\text{.CH(OH).CH}_3$, the anomalous dispersion in which (if not due to polymerisation) may perhaps depend on the concrete existence of two or more of the many varieties of the aromatic nucleus postulated by organic chemists during the past fifty years.

E. Simple and Complex Rotatory Dispersion.

In the preceding pages it has been shown that every case of rotatory dispersion that has been investigated can be represented by means of Drude's equation. Instead of making a distinction between "normal" and "anomalous dispersion," it would be more satisfactory at the present time to distinguish in the first place between *simple rotatory dispersion*, which can be expressed by the equation—

$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2}$$

and *complex rotatory dispersion*, which must be expressed by an equation containing two or more terms, thus:—

$$\alpha = \frac{k_1}{\lambda^2 + \lambda_1^2} + \frac{k_2}{\lambda^2 + \lambda_2^2} + \dots$$

A complex rotatory dispersion may become "anomalous," as R. W. Wood has pointed out, whenever the range of observations covers the region between two absorption bands. This statement includes the anomalous dispersion of Cotton's phenomenon, where the anomaly is observed in the region between an accessible band and an inaccessible band in the remote ultra-violet.

A second form of anomalous dispersion may be produced by two bands on the ultra-violet side of the region under observation, provided that these are associated with rotations of opposite sign. This anomaly is only to be looked for in the case of optical rotations, since negative magnetic rotations are confined to a small range of metallic compounds and have never been detected in optically-active organic compounds.

GENERAL CHARACTERISTICS OF PAPERS PRODUCED FROM HEDYCHUM CORONARIUM.

By CLAYTON BEADLE and HENRY P. STEVENS.

So much practical work has been done in producing papers of different kinds and qualities from this fibre, in many cases on commercial scales in paper mills, and as this fibre has received so much attention at the hands of the paper trade, we think the time has now arrived to refer to these productions somewhat in detail.

The first papers which we produced experimentally were more or less of the Kraft or strong wrapping paper description. As soon as we discovered the cause of the self-sizing we produced papers from parchments to blotting paper. When some papers had been produced on quite a laboratory scale they were reproduced on a small machine as waterleaf, rosin-sized, and some even sized with gelatin. It was soon discovered that the addition of rosin size and alum by way of sizing had no beneficial effect, in fact

alum had a harmful effect. The only beneficial effect could be got in extreme cases, where the whole of the glutinous matter had been removed from the fibre by washing and a sizing result obtained by the addition of rosin and alum. Even here the benefit was doubtful. We soon realised that the proper way of procedure would be to leave all the constituents in, that is if strong sizing and strong paper is required. If softer and more opaque paper is required the addition of some clay will bring about the desired result.

When, however, we resorted to bleaching we made a range of white papers, some of them suitable for fine cigarette papers, others of a softer nature suitable for fine printing, others with excellent bibulous qualities suitable for blottings. Their general appearance is that of good cotton paper. It is not, however, in the direction of bleach fibre that we consider the fibre has its chief value, as we subsequently discovered that there were easier modes of dealing with the fibre.

We ran off some paper on the machine, a portion of which was unbleached, a portion half bleached, and a portion fully bleached. Some of it was unwashed. Portions were washed, run off in the form of waterleaf. To other portions rosin size and alum were added. For the most part the physical qualities of these papers have been described. We produced anywhere from thick substances down to thin silky tissues of 24 grms. to the square metre. These thin tissues, as also some thicker paper 42 grms. to the square metre, had a breaking strain up to 10-11 kilometres in the machine direction—in fact, they are the strongest papers we have so far examined.

On a more extensive scale we produced paper by light boiling in 5 per cent soda with a subsequent bleaching with 5 per cent bleaching powder and very light beating. This was produced at one of the leading paper mills, some of it without anything added, some with rosin size and alum, and the rest, after rosin sizing, was run through a gelatin bath and gelatin sized. All these papers were very excellent. The material was only partially washed in the beater, so the result of the unsized was a semi waterleaf effect. This paper was valued on the market at between £14 and £15 a ton, and is very excellent for small hands, linings, casings, and certain forms of wrappings. A paper made somewhat in this way was thoroughly tested for copying purposes. We found that excellent impressions were obtained in the ordinary way, and it has about the colour, substance, feel, and flexibility required for the manufacture of copying books. By slightly altering our methods, we obtained a silkier feel, such as is obtained with thin Japanese tissues. There is no point in gelatin sizing this class of paper, but it is interesting to note that the web can be passed through a gelatin trough, even when it is a very thin tissue, without giving any difficulty or showing any liability to breakage.

A further trial was made in one of the leading paper mills with a very light boil and light wash in the beater with the roll up for one hour, and the second hour the roll was slightly put down to brush. The paper was put over the paper machine, the stuff was allowed to remain hairy in consequence of the fibro-vascular bundles largely remaining in an unbeaten state. This paper was pronounced equal to and in some respects better than Manila. It was thoroughly tested electrically and physically by a large firm of cable manufacturers, and pronounced to be suitable for the insulation of electric cables. This came as a surprise to us, because when made there was no intention of producing a paper for this purpose. It was quite an afterthought to have it tested in this way. This particular type of hairy *Hedychium* paper has taken on with members of the paper trade. It has a strong look and feel, and handles exceedingly well. It folds and stands the crumpling test as well as any Manila paper, and has good elastic qualities.

Hedychium can be used practically for all kinds of packing papers. It has been made up for bags of different descriptions. Browns of all descriptions have been

made from the commonest to the finest qualities. It is possible to so manipulate the fibre as to produce a dark coloured brown of the ordinary old-fashioned type, or of any grade up to kraft and Manila, without the addition of anything. It comes in for butter papers as well as for cartridge papers. Cutlery papers are a special line usually made from Manila, to which this fibre is well adapted. Bags for bank cashiers are frequently made from Manila; *Hedychium* is equally adaptable. Much of the earlier *Hedychium* paper was made of the greaseproof description. The greaseproof tests were applied to these in comparison with greaseproof papers now upon the market and found to stand all the necessary tests; in fact, it can be made to border upon vegetable parchments. It is also suitable for leather boards, millboards, and mill wrappers.

The paper which stood the crumpling and folding test best was a semitransparent all-*hedychium* machine-made greaseproof paper; it stood six times crumpling and 1000 rubbing, withstanding pinholes; this is an exceedingly severe test.

We have recently studied the question of coloured papers. Generally speaking, the basic dyes and the diamine colours give good results. The following is a list of dyes that have been tested with satisfactory results:—

Yellows.—Papier Yellow, R., G. G., Metanil Yellow, Auramine, Diamine Fast Yellow, Brilliant Yellow.

Red.—Congo, Diamine Scarlet B., Eglantine, Fast Diamine Scarlet 4 B., Saffranine G. extra, Diamine Red, Brilliant Bordeaux R., Brilliant Croceine M. OO.

Black.—Coal Black B., Paper Black T.

Blue.—Diamine Sky Blue F.F., Victoria Blue B., Alizarine Cyanole, Diamine Fast F.F.B., Pure Soluble Blue.

Brown.—Diamine Catechine 3 G., Bismarck Brown F. concentrated, Diamine Brown M.

Green.—Imperial G. 1, Brilliant Green Crystals extra.

Prussian blue has given good results, and on account of the peculiar absorbent nature for mineral matter, it is likely that most of the pigments can be used to advantage. Other trials with pigments are now in progress.

Coming now to the question of paper yarn, which in itself is an important industry, and likely to become more so in the near future, we have already referred to the suitability of *Hedychium* paper for the manufacture of paper yarns on account of its great strength and elasticity. We ran off some reels of *Hedychium* paper some 42 grms. per square metre, and some tissue as thin as 25 grms. These papers were run over paper yarn machines, and the yarn so produced tested in comparison with paper yarns on the machine made from strong Swedish grass. The result was at least equal to the best yarns produced from kraft. The mineral absorbent power of *Hedychium* renders it possible to greatly extend its use.

To sum up, we give an alphabetical list of papers for which *Hedychium* can be used without admixture of other fibres:—

Backing papers. Bag papers of all descriptions. Box boards. Browns of all descriptions. Butter papers. "Caps." Carpet felt papers. Cartridge papers. Casings. Coloured papers. Copyings, Cutlery papers. Duplex papers. Engine boards. Envelope papers (many kinds). Fly papers. Foil papers. Glazed boards. Greaseproof papers. Grocery papers. Hosiery papers. Kraft papers. Leather boards. Manilas. Mill boards. Mill wrappers. Paper yarn. Parchment (imitation). Pin and needle papers. Portmanteau boards. Printings (many kinds). Railway tickets. Sampling papers. "Shops." "Skips." Tea papers. Tissues. Tobacco papers. Toilet papers. Tube papers. Wrappings.

Its use, of course, can be extended by admixture with other materials, but the above would cover a very large market.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

CATS THAT ARE NOT AFFECTED BY THE COLD.

In order to get rid of the multitude of rats that infested the freezing establishments of the town of Pittsburgh, in Pennsylvania, the owners were obliged to procure some cats having a very thick white fur and coming from the Polar regions, for the ordinary domestic cats of the district were paralysed and often died owing to the low temperature of the rooms in which the perishable goods are preserved. These white polar cats, like the white polar bears, seem to resist any degree of cold, however low, and their very thick whiskers make them look very formidable indeed; they are at the same time excellent rat-catchers, so that the depôts of Pittsburg were promptly cleared of their terrible pest.

NEW PETROLIFEROUS BEDS.

A French professor, M. Durandin, has just imagined a somewhat curious method for discovering petroleum beds. M. Durandin does not make any soundings nor preparatory prospections. He only finds out the toponymy of the different localities of a region. He has thus been fortunate enough to discover petroleum where the names of the places recalled the fact that this matter had been known by the natives in former times. In Africa, M. Durandin, by the help of this method, has been able to find out several petroleum beds. He has proceeded in the same way in Indo-China and in Upper Tonkin. In those villages and districts the names of which recalled wax-oil, such as Louang-Prabang, Prof. Durandin has discovered petroleum. This toponymic method has likewise been applied by the gold-seekers when searching for the precious metal. Several localities in France, such as Aurière, St. Sulpice-Laurière, &c., recall by their names the fact that, in these regions there were formerly gold diggings or exploitations.

THE BROMIDES OF THE OCEAN.

Very interesting researches have just been made by M. Louis Chelle, Professor of the Faculty of Medicine of Bourdeaux, concerning sea-water bromides. The different samples of sea-water collected by M. Chelle contain from three to four thousandths of the total quantity of chloride. But the relation of the bromide to the chloride seems to be a constant equal to about four-thousandths for all the seas of the globe, excepting for the Black Sea and for the Baltic. M. Louis Chelle has just searched out in the *Bulletin de l'Institut Océanographique* what is the quantity of bromine contained in the seas and the oceans. As is known, the total of the marine waters of the globe occupies a volume of about 1200 millions of cubic kilometres. These waters containing about the ten-thousandth part of their weight of bromides, it is easy to deduce from this that the totality of oceans contains 120,000 milliards of tons of this salt; that is to say, 80,000 tons per head for each inhabitant of the globe. If then every human being used a kilogram of this salt every year it would take 80 millions of years to use up these reserves. The density of melted bromide of sodium being about 3, the volume of this salt of the sea is represented by 40,000 milliards of cubic metres. If the totality of this salt were uniformly spread over the surface of France (536,408 square kilometres), it would occupy a height of 73 metres. But thus it is easy to appreciate the enormous stock of bromide reserves contained by the Neptunian world.

University of London, King's College, Strand, W.C.—*Advanced Lectures in Chemistry*.—A course of two public lectures on "La Catalyse et mes Divers Travaux sur la Catalyse" will be given by Prof. Paul Sabatier, of the University of Toulouse, on Thursday, May 14, and Friday, May 15, 1914, at 5 p.m.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 2, 1914.

Prof. W. H. PERKIN, LL.D., P.R.S., President,
in the Chair.

THE PRESIDENT announced that the Council have appointed the following Committees for the year 1914—1915:—

Finance Committee—Messrs. E. G. Hooper, G. T. Moody, Sir Edward Thorpe, Sir William A. Tilden, and the Officers.

House Committee—Messrs. Horace T. Brown, R. Messel, J. E. Reynolds, J. M. Thomson, Sir William A. Tilden, and the Officers.

Library Committee—Messrs. B. Dyer, W. Gowland, A. Harden, J. T. Hewitt, C. A. Keane, A. R. Ling, T. M. Lowry, R. Meldola, E. J. Mills, J. M. Thomson (Chairman), Sir William A. Tilden, J. A. Voelcker, the Editor, and the Officers.

Publication Committee—Messrs. H. B. Baker, J. N. Collie, F. G. Donnan, B. Dyer, M. O. Forster, T. M. Lowry, F. B. Power, G. Senter, and the Officers.

Research Fund Committee—Messrs. H. B. Baker, W. R. Bousfield, Horace T. Brown, H. B. Dixon, J. J. Dobbie, F. G. Donnan, M. O. Forster, P. F. Frankland, W. J. Pope, W. Palmer Wynne, and the Officers.

Messrs. S. Bate, A. H. Hay, and F. A. Pickworth were formally admitted Fellows of the Society.

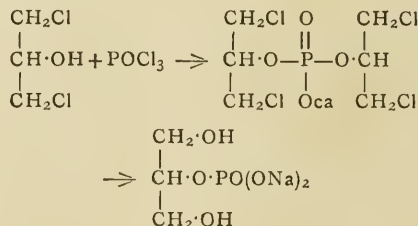
Certificates were read for the first time in favour of Messrs. Nicholas Alexander Auflogoff, c/o The London and Thames Haven Oil Wharves, Ltd., Thames Haven, Essex; Harry Berry, The Northern College of Pharmacy, Burlington Street, Manchester; Stanley Winter Collins, B.Sc., 1, Tideswell Road, Putney, S.W.; Herbert William Cremer, B.Sc., Preston Lea, Faversham; Leonard Eric Hinkel, B.Sc., Bucklands, Old Oak Road, Acton, W.; John Orron Leighton, 30, Albany Street, Hull; Ernest Ferguson Pollock, Ph.D., Kirkland, Bonhill, Dumbartonshire; Charles Edward Roberts, B.A., B.Sc., St. John's College, Cambridge.

Certificates have been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Messrs. Edward Godfrey Bryant, B.A., B.Sc., Grey Institute, Port Elizabeth, S. Africa; Alfred Cornwell Harrison, Penhalonga, Rhodesia, S. Africa.

Of the following papers those marked * were read:—

*92. "The Constitution of the Glycerylphosphates. The Synthesis of α - and β -Glycerylphosphates." By HAROLD KING and FRANK LEE PYMAN.

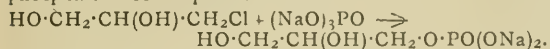
Pure salts of α - and β -glycerylphosphoric acids have been prepared. For the preparation of the β -salts, a dichlorohydrin was combined with phosphoryl chloride (compare Tutin and Hann, *Trans.*, 1906, lxxxix., 1749), giving calcium bis-*s*-dichloroisopropylphosphate, which on hydrolysis with sodium carbonate yielded sodium β -glycerylphosphate,—



This salt was identical with Poulenc's crystalline sodium glycerylphosphate of commerce, which must consequently be the β -salt. The identity of the two salts was confirmed

by the comparison of the properties of the calcium, barium, brucine, and quinine salts prepared from each of them.

An attempt to prepare the α -salts in an analogous manner was unsuccessful, but these salts were readily obtained by the action of α -monochlorohydrin on trisodium phosphate in cold aqueous solution:—



Several salts of the α -acid were prepared and characterised.

The results of previous investigators were discussed.

DISCUSSION.

Dr. PLIMMER asked Dr. Pyman how the analyses of the glycerolphosphates, which he described, had been effected. In his experience of the analysis of organic phosphorus compounds, the values obtained for carbon, by combustion by both dry and wet methods, were always too low.

*93. "The Viscosity of Sulphuric Acid." By ALBERT ERNEST DUNSTAN.

Some years ago (Dunstan and Wilson, *Trans.*, 1907, xci., 85) a series of determinations of the viscosities of aqueous sulphuric acid solutions at 25° was undertaken with the object of finding the maximum point. Owing to the kindness of Prof. A. F. Joseph, it was discovered that a constant numerical error had been made in calculating the values of the viscosity coefficients. Consequently, the numbers given on p. 85 of the above reference should be multiplied by 0.2325.

In the meantime, several papers have appeared on the viscosity of sulphuric acid, and as the results apparently fall on two distinct curves, it was thought desirable to repeat some of the measurements, both at 25° and at other temperatures, and to ascertain which of these two sets of results is the more accurate.

The figures up to date are as follows:—

Observer and reference.	Viscosity.	Temp.
Kremann and Ehrlich (<i>Monatsh.</i> , 1907, xxviii., 831)	0.618	0.0°
Drucker and Kassel (<i>Zeit. Phys. Chem.</i> , 1911, lxxvi., 373)	0.4843	0.0°
Poiseuille (<i>Ann. Chim. Phys.</i> , 1843, [2], vii., 50)	0.3195	11.2°
Drucker and Kassel (<i>loc. cit.</i>)	0.2694	15.0°
Graham (<i>Phil. Mag.</i> , 1862, xxiv., 238)	0.2193	20.0°
Bergius (<i>Zeit. Phys. Chem.</i> , 1910, lxxii., 357)	0.1915	25.0°
Pound (<i>Trans.</i> , 1911, xcix., 708)	0.210	30.0°
Kremann (<i>loc. cit.</i>)	0.172	33.0°
Kremann (<i>loc. cit.</i>)	0.076	63.5°
Drucker (<i>loc. cit.</i>)	0.0503	76.5°

The values found by Kremann and Ehrlich and by Pound lie well above those of Drucker, Graham, and Poiseuille.

In the experiments here recorded, the strength of the sulphuric acid was determined by gravimetric and volumetric methods, and also by means of the densities of its diluted aqueous solutions.

The mean of eight concordant analyses was 100.3 per cent (calculated as H_2SO_4), with a mean error of 0.2 per cent.

The method which was adopted for obtaining values of the viscosity of the 100 per cent acid consisted in interpolating on a viscosity-concentration curve ranging from 96 to 100.3 per cent.

The results are as follows:—

Temperature.	Viscosity of—			
	100.3 per cent H_2SO_4 .	99.8 per cent H_2SO_4 .	98.2 per cent H_2SO_4 .	96 per cent H_2SO_4 .
13.8°	0.371	0.342	—	—
25.0°	0.239	0.224	0.220	0.190
50.0°	0.109	0.102	0.0954	0.0943
70.0°	0.0632	0.0657	0.0598	—
90.0°	0.0433	0.0410	0.0403	0.0399

whence for the 100 per cent acid:—

Temperature.	Viscosity.
13.8°	0.360
25.0°	0.235
50.0°	0.106
70.0°	0.0635
90.0°	0.0425

The value thus found at 25° is rather less than that which was previously obtained, but it will be seen that the new values agree excellently with those of Kremann.

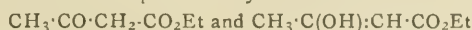
*94. "Tautomerism, Desmotropy, and Dynamic Isomerism." By THOMAS MARTIN LOWRY.

The question asked by Prof. Meldola at the close of the President's Address to the Annual General Meeting of the Chemical Society suggests that a short statement in reference to the nomenclature of the subject might be welcomed by some Fellows who have not had an opportunity of consulting the earlier literature.

Briefly, it may be said that all the essential facts in reference to the conception of *equilibrium between isomerides*, as described so lucidly by the President in his Address, are set out in Butlerow's classical, but almost forgotten, paper "Ueber Isodibutylene" (*Annalen*, 1877, clxxxix., 44). They were applied by him to explain the behaviour of substances such as cyanic and hydrocyanic acids, which yield two series of derivatives; these were regarded by Butlerow as mixtures of isomerides in equilibrium, to which no definite formula could be assigned, "since molecules of two or more isomeric varieties would always be present." The name *dynamic isomerism* was introduced in 1899 (*Trans.*, lxxv., 235), as a paraphrase of Butlerow's description of "a condition of equilibrium depending on incessant isomeric change"; but the adjective *isodynamic* had already been suggested by Armstrong in 1889 (Watts' Dictionary, "Isomerism") to describe those isomerides "which change their type with exceptional facility in the course of chemical interchanges." The word *metameric* had been used in this sense in 1833 by Berzelius to describe isomerides which were readily converted into one another, but the usefulness of the word was destroyed by a misguided attempt to transfer it to another usage.

The hypothesis of *tautomerism* was introduced by Laar in 1885 (*Ber.*, xviii., 648) to account for the facts which had already (as time has shown) been explained adequately by Butlerow. The clearest statement of what tautomerism means, however, is found in a subsequent paper (*Ber.*, 1886, xix., 730), in which Laar sets out the points in which his views differ from those of Butlerow. Laar asserts that, in every case of tautomerism, the different formulæ suggested by the reactions of the substance represent, "not isomeric, but identical bodies"; the term cannot, therefore, be applied to any case of isomerism, however readily the isomerides may be converted into one another. Further, he repudiates the chemical analogy of dissociation, which Butlerow had suggested, and quotes instead the views of Maxwell and of Wiedemann on the molecular vibrations which give rise to light.

It is impossible to say whether tautomerism exists; but it has at least been proved by the work of Knorr that the two substances represented by the formulæ—



are not tautomeric, but have a real existence as well-defined isomeric compounds, which only change into one another under definite physical and chemical conditions. They have, in fact, a right to be described as isomerides, in just the same sense as ammonium cyanate and carbamide, two fortunate compounds which have hitherto escaped condemnation, although equally guilty of undergoing reversible isomeric change and of yielding two series of derivatives.

The word *desmotropy* was introduced by Jacobson (*Ber.*, 1887, xx., 1732, footnote; 1888, xxi., 2628, footnote) in 1887, when it had become evident that Laar's theory of

tautomerism had broken down completely in the very case to which it had been most frequently applied, namely, the labile isomerism which results from the contiguity of a double bond and an acidic hydrogen atom. Jacobson adopted the view "that the known forms of such compounds are to be represented by a definite grouping of atoms, which in certain reactions passes over into an isomeric grouping by a rearrangement of bonds consequent upon the displacement of a hydrogen atom"; it was to express this view that the word "desmotropy" was introduced. If used in this sense, to describe the labile isomerism produced by the mobility of a hydrogen atom, it might be of real value; unfortunately, the meaning of the word was tampered with by Hantzsch and Hermann (*Ber.*, 1887, xx., 2802), and, as an inevitable consequence, it has become ambiguous, and has ceased to be clearly significant.

DISCUSSION.

Dr. FORSTER expressed regret that Dr. Lowry's remarks failed to clear up the confusion attending the words in question. Having stated that no case of genuine tautomerism exists, and that he deplored the association of an incorrect meaning with any word, Dr. Lowry might have declared that, in his opinion, use of this word should be discontinued. In Dr. Forster's view, the word isodynamic was unsuitable, because it suggested equal, or similar, force or motion, whereas one of the commonest features of such pairs is that one member changes far more rapidly than the other.

Dr. LOWRY replied that the word "tautomeric" should be withdrawn in all cases of proved isomerism, and might with advantage be abandoned altogether by those who no longer accepted Laar's hypothesis. The familiar words "isomerism" and "isomeric change" should be used whenever they expressed the essential facts; if these were not sufficient, the term "dynamic isomerism" might be used to distinguish the more labile varieties of isomerism; in view of the difficulty of re-introducing the word "metameric" in its original sense, the labile compounds themselves were best described as "isodynamic," for example, the two substances isolated by Knorr could be referred to as "isodynamic forms" of the ester.

95. "*The System: Ethyl Ether—Water—Potassium Iodide—Mercuric Iodide.* Part III. *Solutions Unsaturated with respect to Solid Phases in the Four-component System.*" By ALFRED CHARLES DUNNINGHAM.

Liquids unsaturated with respect to solid phases can exist either as one, two, or three layers.

Curves have been determined experimentally for the series of three conjugate liquids, and from these the nature of the equilibria underlying the formation of three layers has been deduced.

The conditions under which two and three layers can separate in the system were fully discussed.

96. "*The Velocity of Saponification of the Acyl Derivatives of the Substituted Phenols.* Part I. *Phenyl Benzoate.*" By HAMILTON MCCOMBIE and HAROLD ARCHIBALD SCARBOROUGH.

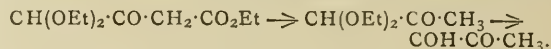
The velocity of saponification of phenyl benzoate by alcoholic potassium hydroxide at 30° has been studied with reference to the influence of the initial concentration of both the ester and the alkali.

The value of K was found to be independent of the initial concentration of either of the reacting substances, a mean value, $K=0.00428$, being obtained as the result of five series of determinations, each series representing twenty-five readings.

The reaction, as a whole, was found to be bimolecular; the van't Hoff and Noyes equations for determining the order of the reaction proved that the reaction was unimolecular with regard to the initial concentration of the ester or the alcoholic potassium hydroxide.

97. "*A General Method for the Preparation of Glyoxals and their Acetals.*" By HENRY DRYSDALE DAKIN and HAROLD WARD DUDLEY.

Ethyl diethoxyacetate and ethyl acetate react smoothly with sodium to give ethyl γ -diethoxyacetoacetate. The latter substance on hydrolysis with potassium hydroxide gives the acetal of methylglyoxal. Methylglyoxal is obtained from the acetal by hydrolysis with dilute sulphuric acid.



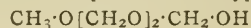
Ethyl γ -diethoxyacetoacetate readily yields mono and di-alkyl derivatives on successive treatment with sodium and alkyl haloids, thus furnishing a convenient method for the preparation of new substituted γ -diethoxyacetoacetic esters, alkylglyoxals, and their corresponding acetals. The following substances have been prepared:—

Ethyl γ -diethoxy- α -methylacetoacetate, ethylglyoxal and its acetal; ethyl γ -diethoxy- α -dimethylacetoacetate, isopropylglyoxal and its acetal; ethyl γ -diethoxy- α -methyl- α -ethylacetoacetate, sec.-butylglyoxal and its acetal; ethyl γ -diethoxy- α -isopropylacetoacetate; isobutylglyoxal and its acetal; ethyl γ -diethoxy- α -benzylacetoacetate, phenylethylglyoxal and its acetal.

The reactions of ethyl γ -diethoxyacetoacetate are still under investigation.

98. "*The Action of Sulphuric Acid on Paraformaldehyde.*" By JOHN GUNNING MOORE DUNLOP.

When paraformaldehyde is heated for twenty-four hours in a sealed tube with a little sulphuric acid at 115–120°, the contents are converted into a liquid, which on distillation gives two fractions. One of these is methyl formate, and the other, which boils at 90–100°, is found to contain hydroxymethyl ether, $\text{CH}_3\text{O} \cdot \text{CH}_2\text{OH}$, and somewhat indefinite compounds of the type—



(compare Reychler, *Bull. Soc. Chim.*, 1907, [iv], i., 1189).

Since the paraformaldehyde was shown to be free from methyl alcohol, the latter must have resulted from the decomposition of the methyl formate, which in turn is derived from the condensation of two molecules of formaldehyde.

99. "*The Destructive Distillation of Soil.*" (Preliminary Note.) By ERIC JOHN HOLMYARD.

With a view to obtain further insight into the nature of the organic matter in soil, various soils have been destructively distilled from an iron retort. At a temperature of low redness, a distillate of two layers was obtained; the lower, aqueous, layer was strongly alkaline, and smelt of ammonia. The upper layer consisted of small quantities of a brown oil, possessing a characteristic odour resembling that of pyridine. Qualitative tests on the aqueous layer showed the presence of phenol and ammonia. The oil, after the addition of alkali, was purified by distillation in a current of steam, and was then pale yellow. On exposure to air for some days it darkened. Qualitative tests indicated the presence in it of pyridine, quinoline, pyrrole, indole, thiophen, and possibly furfuraldehyde.

Both field soils and garden soils give similar results, although the yield of oil was greater in the case of the garden soils.

The results are consistent with the view that the processes of decomposition occurring in the organic matter in soil are similar to those operative in the formation of coal. Further experiments on the subject are in progress.

100. "*Dibenzoylglucoxylose, a Natural Benzoyl Derivative of a New Disaccharide.*" By FREDERICK RELDING POWER and ARTHUR HENRY SALWAY.

The crystalline compound *dibenzoylglucoxylose* (m. p. 147–148°), $\text{C}_{11}\text{H}_{18}\text{O}_{10}$ ($\text{CO} \cdot \text{C}_6\text{H}_5$)₂· H_2O , which represents the bitter constituent of the leaves and stems of *Daviesia latifolia*, R. Br. (*Trans.*, 1914, cv., 772), has now been completely examined with respect to its properties, and those of the disaccharide (*glucoxylose*) which it yields by its primary hydrolysis.

101. "The Molecular Weights of some Salts of the Alkali Metals and an Account of the Compounds of these Salts with the Alcohols." By WILLIAM ERNEST STEPHEN TURNER and CRELYN COLGRAVE BISSETT.

The results of an investigation (shortly to be published) on the influence of the solvent on the molecular weights of salts (Turner and Pollard) have been applied to interpret the behaviour in solution of the salts of the alkali metals, more particularly those with the halogen elements, and it was argued that the non-associated state of these salts found by several previous workers could be satisfactorily accounted for by the influence either of the dielectric character of the solvent or of the temperature of the determination.

In the series of alcohols—ethyl, isobutyl and isoamyl—it was demonstrated that the molecular weights of lithium chloride, bromide, iodide, and nitrate rise as the dielectric constant of the solvent falls. The complication arising through the combination of solvent and solute was discussed, and the five possible types of behaviour owing to concurrent association and chemical combination were illustrated. Association is most pronounced with lithium nitrate, which does not enter into combination with the solvents employed. The associated character of the lithium salts was demonstrated further by molecular-weight determinations in acetic acid.

The lithium haloids combine with the alcohols to form compounds $\text{LiCl}(\text{Br}, \text{I}), 3\text{MeOH}$ and $\text{LiCl}(\text{Br}, \text{I}), 4\text{ROH}$, where R may be the ethyl, *n*-propyl, isobutyl, or isoamyl radicle. The compounds $\text{NaI}, 3\text{MeOH}$ and $\text{NaI}, 3\text{CH}_3\text{CO}_2\text{H}$ were also isolated.

102. "Consistent Molecular Formulae." By WILLIAM ERNEST STEPHEN TURNER.

From the point of view of Avogadro's hypothesis, it was argued that many of the common molecular formulae still in use, such, for example, as H_2 , I_2 , P_4 , SnCl_2 , and $\text{C}_2\text{H}_4\text{O}_2$, cannot be regarded as derived consistently, nor can they, as the outcome of modern work, be considered as adequate.

When molecular weights are derived from measurements in solution, an additional factor is introduced in the effect of the solvent, rendering a complete comparison with vapour-density determinations impossible. The conditions to be observed in order to make the comparison as favourable as possible were discussed.

It was argued that the molecular weight of a substance is, in most cases at any rate, a property dependent on temperature, pressure, and the medium, just as any other physical property, and that, in consequence, the only satisfactory mode of writing molecular formulae is by a formula X_n , in the case of elements, or $(\text{XY})_n$ for compounds, where *n* is to be given the value which holds for the particular conditions of existence.

For some substances, *n* remains constant over a wide range. Thus, for hydrogen, *n*=2 over a wide range of conditions, but at a very high temperature may become 1. For sulphur, this variation extends from *n*=8 to *n*=1.

The use of molecular formulae in the way advocated would emphasise the connexion between the chemical and physical properties and the molecular weight.

103. "Note on the Formation of Triphenylcarbinol." By MAURICE COPISAROW.

Friedel and Crafts (*Comptes Rendus*, 1877, lxxxiv., 1452; *Ann. Chim. Phys.*, 1884, [vi], 1, 500) found that on distilling the condensation product obtained from carbon tetrachloride and benzene in the presence of aluminium chloride triphenylmethane was chiefly produced, along with some triphenylcarbinol and possibly tetraphenylmethane.

E. and O. Fischer (*Annalen*, 1878, cxciv., 254), repeating Friedel and Crafts' experiment in the same manner, obtained chiefly triphenylmethane and a little triphenylcarbinol, but failed to detect any tetraphenylmethane.

Hinsberg (*Ber.*, 1899, xxxii., 2422), replacing aluminium chloride by ferric chloride in the condensation of carbon

tetrachloride with benzene, found the product, on distillation in a current of steam, to consist of triphenylcarbinol only.

The question arises whether the difference in the products is due to the dissimilar experimental conditions or to the different effect of the metallic chlorides. In order to decide this, the author has performed the following experiments:—

(1) Sixteen grms. (1 mol.) of carbon tetrachloride were mixed with 25–30 grms. (3–4 mols.) of benzene, and 250 cc. of carbon disulphide added; 45 grms. of aluminium chloride were gradually introduced, the reaction being allowed to cease after each portion before further addition. The mixture was heated on the steam-bath for about nine hours, and afterwards decomposed with ice and hydrochloric acid, the carbon disulphide removed, and the product subjected to distillation with steam. The residue, a dark solid mass, was dissolved in alcohol, from which triphenylcarbinol crystallised; the latter was dissolved in benzene, the solution boiled with animal charcoal, and filtered, when, on cooling, large, white, rhombic crystals of triphenylcarbinol, melting at 159° , were obtained. The yield was 19 grms.

(2) Hinsberg's experiment (*loc. cit.*) was repeated, but the product was submitted to distillation as described by Friedel and Crafts. The product was found to consist chiefly of triphenylmethane (m. p. 92°) and a small amount of triphenylcarbinol.

From these experiments the conclusion may be drawn that aluminium chloride is identical in its effect with ferric chloride, but being more energetic it is to be preferred, as it gives better yields and requires less time to complete the reaction.

The real difficulty in obtaining very good yields is in the large amount of tarry matter formed during the reaction.

The difference in the products obtained by Friedel and Crafts and E. and O. Fischer on the one hand, and by Hinsberg on the other, is due to the secondary effect during the distillation without steam in the former case.

No tetraphenylmethane was detected in the author's experiments.

104. "The Ionisation of Acids and their Activity as Catalysts." By HARRY MEDFORTH DAWSON.

Recent experiments (Dawson and Powis, *Trans.*, 1913, ciiv., 2135) have shown that the rate of isomeric change of acetone in dilute aqueous solution under the catalytic influence of acids can be represented by the equation $v = k_{\text{H}}ca + k_{\text{M}}c(1-a)$, in which *v* is the reaction velocity, *c* the concentration of the acid, *a* its degree of ionisation, and k_{H} and k_{M} are the activity-coefficients for the ionised and non-ionised acids respectively. For hydrochloric acid, the degree of ionisation employed in the calculation was that yielded by conductivity data, whilst for dichloroacetic, *α*,*β*-dibromopropionic, chloroacetic, and acetic acid the value of *a* was calculated from the ionisation-coefficient, $K = ca^2/(1-a)$.

According to Wegscheider (*Zeit. Phys. Chem.*, 1909, lxi., 603), the mass-action equation is no longer satisfied by the conductivity data if the ionic concentration exceeds a certain limiting value. Empirical formulae connecting the degree of ionisation and the concentration have been suggested by Kraus and Bray (*Journ. Amer. Chem. Soc.*, 1913, xxxv., 1315) and by Kendall (*Trans.*, 1912, ci., 1275), which take into account the inter-ionic action which is supposed to give rise to the increase of $ca^2/(1-a)$ in solutions of higher concentration.

Assuming that the deviations from the mass law which are indicated by these empirical equations are true deviations, it is somewhat surprising to find such a close agreement between the observed and calculated reaction velocities when the value used for the degree of ionisation is that calculated on the basis of the mass law.

According to Kendall (*loc. cit.*, p. 1295), the ionisation of dichloroacetic acid can be represented by the formula

$c\beta/(1-\beta) = 0.0316 + 0.080(1-\beta)/\beta$, where β is the degree of ionisation at concentration c . If the values of β given by this formula are substituted in the equation $v = k_H c\beta + k_M c(1-\beta)$, the combination of the two extreme solutions ($c = 0.01$ and 0.2) gives $k_H = 462$ and $k_M = 126$, whereas the α values derived from the mass action formula yield $k_H = 445$ and $k_M = 203$. Both pairs of coefficients give almost equally good results in so far as the agreement between the observed and calculated velocities for acid solutions of intermediate concentration is concerned. This is shown in the following table, in which the first column gives the concentration of the acid, the second and third the values of α and β , the fourth and fifth the corresponding calculated velocities v_a and v_β , and the sixth the observed velocity, v .

Dichloroacetic Acid.

c .	α .	β .	v_a .	v_β .	v .
0.01	0.856	0.845	(4.10)	(4.10)	4.10
0.02	0.769	0.778	7.79	7.75	7.95
0.05	0.621	0.675	17.7	17.65	18.1
0.1	0.503	0.593	32.5	32.5	32.7
0.2	0.393	0.512	(59.6)	(59.6)	59.6

According to the results in this table, there is nothing to choose between α and β values for the degree of ionisation. It should be noted, however, that the reaction velocities under v_β are calculated on the basis of a coefficient $k_H = 462$, which deviates appreciably from the coefficient $k_H = 437$ derived from the data for hydrochloric acid. The divergence is greater than that shown by any one of the k_H values which are obtained from the data for the four weaker acids on the assumption that the ionisation occurs in accordance with the mass law. The agreement between the separate values of k_H (*loc. cit.*, p. 2142) is the more remarkable when the difference in the ionic concentration of the solutions used is taken into account.

From the above comparison, it is evident that the degree of ionisation of acids in relatively concentrated solutions must be determined with greater precision before it is possible to assign final values to the activity-coefficients of the non-ionised acids. Experiments with this object in view are in progress.

105. "Synthesis of dl-Tyrosine and dl-3:4-Dihydroxyphenylalanine." By HENRY STEPHEN and CHARLES WEIZMANN.

In continuation of previous work (*Proc.*, 1912, xxviii., 147), the authors have obtained the following new substances, in addition to those already mentioned in the above note:—

Phthalamino-p-methoxybenzylmalonic acid, obtained by hydrolysing ethyl phthalimino-*p*-methoxybenzylmalonate, is a white powder crystallising from acetic acid in plates, and melting and decomposing at 210° .

Phthalaminopiperonylmalonic acid, obtained from the corresponding condensation product, melts and decomposes at 234° . On hydrolysis with hydrochloric or hydrobromic acid, the *hydrochloride* (m. p. 246°) or *hydrobromide* (m. p. 212°) of 3:4-dihydroxyphenylalanine is obtained.

106. "Optically Active Derivatives of d-Dimethoxy- and d-Diethoxysuccinic Acids." By CHARLES ROBERT YOUNG.

The preparation of methyl d-diethoxysuccinate was described; the specific rotation of the pure liquid was found to be almost identical with that of the isomeric ethyl d-dimethoxysuccinate.

The optically active anilic acids, anils, anilides, and hydrazides derived from d-dimethoxy- and d-diethoxysuccinic acids have been prepared, and their rotatory powers compared. No evidence of the formation of isoanils was obtained.

d-Dimethoxysuccinamic acid and the corresponding imide were also prepared, and the latter was converted into its methyl derivative by alkylation with silver oxide and methyl iodide.

107. "Rate of Evolution of Gases from Supersaturated Solutions. Part II. Carbon Dioxide in Solutions of Gelatin and Starch." By ALEXANDER FINDLAY and GEORGE KING.

In continuation of the previous investigation (*Trans.*, 1913, ciii., 1170), it was shown that the rate of escape of carbon dioxide from solutions of gelatin and of starch is markedly affected, and more especially so in the case of dilute solutions, by the method of treatment of the solution. The shorter the time during which the solutions are boiled (to remove air), and the more rapid the cooling of the boiled solutions, the greater is the influence of the colloidal solution on the rate of escape of gas. The results obtained, more especially in the case of solutions of gelatin, lead to the conclusion that the difference in the behaviour of such solutions, as compared with water, is due, mainly, to the concentration of the gelatin sol, and not to the presence of the gel.

108. "The Oxidation of Carbohydrates and Related Substances by means of Potassium Persulphate." By JOHN KERFOOT WOOD and NELLIE WALKER.

The authors have made a comparative study of the rates of oxidation of a number of carbohydrates and kindred substances by potassium persulphate in the presence of silver sulphate. In the absence of the silver salt the reaction proceeds very slowly, but the addition of small quantities of a 0.5 per cent solution of silver sulphate produces a marked acceleration of the process of oxidation. The experiments were conducted at 25° , and the solution of persulphate was almost saturated at that temperature. Equivalent amounts of the carbohydrates were employed, and sufficient of the persulphate solution to supply 1 atom of oxygen per molecule of carbohydrate was added. (With disaccharides, 1 atom of available oxygen per half molecule of sugar was added). The reaction was followed by removing portions of the mixtures from time to time, and measuring the acidity of the solution. Velocity-constants were calculated by means of the bimolecular formula. The results show that galactose, arabinose, and xylose are all oxidised at about the same rate; the velocity of oxidation of dextrose is slightly lower than in the case of the three sugars mentioned, whilst the rate for rhamnose is a little lower than that for dextrose. The authors consider that in the case of these five sugars it is extremely probable that under the conditions employed the sugars are almost quantitatively converted into the corresponding aldonic acids.

The velocity of oxidation of laevulose is greater than that of dextrose, and the process does not appear to be of so simple a character.

The disaccharides are oxidised more rapidly than the simple sugars.

With the polyhydric alcohols it was impossible to obtain, in the majority of cases, a definite velocity-constant. This indicates the occurrence of secondary reactions, the alcohol probably being partly converted into an aldehyde, which is then more rapidly oxidised than was the original substance.

109. "Allanturic Acid." By ARTHUR WALSH TITHERLEY and NOEL GUILBERT STEVENSON COPPIN.

The syrup described as allanturic acid in the literature, obtained by the decomposition of allantoin by hot aqueous nitric acid and by other means, has been shown by the authors to be a mixture the composition of which is dependent on its origin, the essential constituents being carbamidoglycollic acid, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, its

lactam, glyoxalylcarbamide, $\begin{array}{c} \text{CO} \text{---} \text{NH} \\ | \\ \text{CH}(\text{OH})\cdot\text{NH} \end{array} \text{CO}$, and a

very weak base, $\text{C}_3\text{H}_5\text{O}_2\text{N}_3$, may also be present.

The syrup obtained from allantoin and nitric acid by Pelouze, and later by Mulder, has been closely studied. On treatment with acetone, it falls to a white powder containing about 60 per cent of glyoxalylcarbamide, the remainder being chiefly the compound $\text{C}_3\text{H}_5\text{O}_2\text{N}_3$, partly

present as nitrate. Since the latter dissociates on dissolving in water, giving free nitric acid, the powder appears to possess pronounced acid properties, but the glyoxalyl-carbamide component is itself only a pseudo-acid requiring about 40 per cent of an equivalent of alkali to show a neutral point (indefinite) to phenolphthalein in dilute aqueous solution. The "glyoxalylcarbamide" of Medicus cannot, on account of its properties and mode of formation be this lactam, and the present investigation throws no light on its nature.

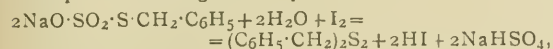
Evidence bearing on the nature of "allanturic acid" has been obtained by a study of the decomposition of allanturic acid by nitric acid under varying conditions. At 0° or 15° with concentrated nitric acid, 1 molecule of carbamide is eliminated, and after concentration in a vacuum in the cold, a syrup or amorphous solid is obtained, consisting of glyoxalylcarbamide and the nitrate of a carboxylic acid, probably carbamidoglycollic acid,—



With aqueous nitric acid at 100° the decomposition is complete in a few minutes, but less than 1 molecule of carbamide is split off, and ammonia is eliminated. On now (1) concentrating in a vacuum and treating the syrup with acetone, impure glyoxalylcarbamide is obtained in small yield, but on (2) concentrating at 100° carbon dioxide is eliminated, and the syrup with acetone gives a relatively large yield of glyoxalylcarbamide admixed with the nitrate of the base, $\text{C}_3\text{H}_5\text{O}_2\text{N}_3$. These facts indicate that the allanturic acid decomposes in two ways, namely, (a) by hydrolysis, yielding carbamide and carbamidoglycollic acid, which during concentration suffers incomplete conversion into glyoxalylcarbamide; (b) by elimination of ammonia, yielding 4:6-diketohexahydro-1:3:5-triazine-2-carboxylic acid, which at 100° in the presence of nitric acid loses carbon dioxide, and furnishes 4:6-diketohexahydro-1:3:5-triazine (the weak base $\text{C}_3\text{H}_5\text{O}_2\text{N}_3$).

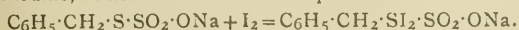
110. "The Reaction between Sodium Benzylthiosulphate and Iodine." By THOMAS SLATER PRICE and ARTHUR JACQUES.

The velocity of the reaction between sodium benzylthiosulphate and iodine in potassium iodide solution, which takes place according to the equation:—



has been investigated in aqueous solution at 25°. Experiments with either component in excess showed that the reaction is unimolecular, both with respect to the sodium benzylthiosulphate and with respect to the free iodine; apparently the tri-iodide ion does not enter into reaction. When the components are present in equivalent concentrations, the velocity-constants are satisfactory in the more concentrated solutions, but rise continuously in the more dilute solutions; moreover, the value of the constants varies in the different solutions. The rise and variation in the constants were discussed and shown to be due, in all probability, (1) to the catalytic influence of the precipitated benzyl sulphide, owing to adsorption of iodine; (2) to the fact that the anion of the sodium benzylthiosulphate is alone concerned in the reaction.

The first stage in the reaction is probably the combination of a molecule of sodium benzylthiosulphate with one of iodine, in accordance with the equation:—



The compound thus produced is then decomposed very quickly, with the formation of benzyl disulphide, sodium hydrogen sulphate, and hydriodic acid.

111. "The Dynamics of the Action of Halogens on Aliphatic Aldehydes. Keto-enol Isomerism of the Aldehydes." By HARRY MEDFORTH DAWSON, DONALD BURTON, and HARRY ARK.

Kinetic experiments relating to the action of bromine and iodine on acetaldehyde and its homologues have been made in dilute aqueous (or aqueous-alcoholic) solution, in

which the rate of disappearance of the halogen was measured. The majority of the observations were made with acetaldehyde, and in all cases the aldehyde was present in relatively large quantity compared with the halogen.

The results obtained indicate that oxidation and substitution may both occur in the action of bromine on the aldehydes in dilute aqueous solution. Whereas in neutral solution the whole of the bromine is used up in the oxidation of the aldehyde, substitution takes place simultaneously if the solution is rendered strongly acid by the addition of a mineral acid. The relation between the quantities of bromine, which are used up in oxidation and substitution respectively, depends on the concentration of the free bromine and on the acidity of the solution. In a N-hydrobromic acid solution the concentration of free bromine is only about one-twentieth of the total bromine-concentration as a consequence of the formation of polybromide (HB_3), and in these circumstances it was found that the substitution reaction is the predominant reaction, whereas oxidation is predominant in a N-hydrochloric acid, and still more so in a N-sulphuric acid solution.

In neutral solution, iodine reacts with acetaldehyde very slowly, but the rate of disappearance of the halogen is greatly increased in the presence of a mineral acid. The reaction velocity in acid solution is nearly constant, and the velocity-coefficient is practically identical with the coefficient calculated for the substitution reaction from the data obtained in the experiments with bromine.

The experimental facts suggest that halogen substitution in the aldehydes is conditioned by preliminary isomeric transformation of the aldehyde from the ketonic to the enolic form, the velocity of this change being greatly increased in the presence of acids.

112. "Equilibrium in the System: Ethyl Alcohol, Acetic Acid, Ethyl Acetate and Water, and its Apparent Displacement by Mineral Chlorides." By JAMES FLETCHER and WILLIAM JACOB JONES.

It has already been shown (*Trans.*, 1911, xcix., 1427) that hydrogen chloride disturbs the above equilibrium owing to the formation of hydrate. In the present investigation these observations have been extended so as to include lithium and calcium chlorides.

113. "The Mechanism of Cyanidion Catalyses." By WILLIAM JACOB JONES.

A chemico-dynamical investigation of the interaction between hydrogen cyanide and certain organic anions containing a double bond was described. It was shown that the speed of addition was proportional to the concentration of cyanidion present.

114. "The Interaction between Hydrogen Cyanide and Aldehydes and Ketones in Dilute Solution." By WILLIAM JACOB JONES.

It was shown that in dilute solution equilibria of the type $\text{RR}'\text{CO} + \text{HCN} \rightleftharpoons \text{RR}'\text{C}(\text{OH})\cdot\text{CN}$ are established. Water and, to a less extent, alcohol exert a dissociative influence on cyanohydrins.

Oxalacetic Acid.—H. Gault.—Oxalacetic ether is very readily prepared by the condensation of oxalic ether with acetic ether in presence of sodium or sodium ethylate. When distilled it is not stable, but alters more or less rapidly even at the ordinary temperature, undergoing progressive lactonisation. Under the action of heat the proportion of lactone formed amounts to 70–80 per cent at 150°. Hence it is necessary to avoid overheating during distillation. It also lactonises when left in contact with dilute solutions of potassium carbonate or bicarbonate. Oxalacetic ether has characteristic acid properties, readily yielding, for example, the corresponding potassium salt with concentrated solutions of potassium carbonate or bicarbonate.—*Comptes Rendus*, clviii., No. 10.

NOTICES OF BOOKS.

Indiarubber Laboratory Practice. By W. A. CASPARI, B.Sc. (Vict.), Ph.D. (Jena), F.I.C. London: Macmillan and Co., Ltd. 1914.

As representing the results of the author's ten-year-long experience of rubber analysis this little book has a certain value. It does not aspire to be an exhaustive or critical treatise, but rather to be a strictly practical manual in which the chemist engaged in rubber analysis may find some useful hints. In it the analysis of crude and of manufactured rubbers are treated fairly fully, and the apparatus used for the various experiments is described and illustrated. No theoretical questions are discussed, and mechanical methods of testing are not included. On the whole, the book seems likely to serve its purpose, and chemists who have had a good general training in analytical work will with its aid be able to cope with the special case of rubber analysis.

The Pigments and Mediums of the Old Masters. By A. P. LAURIE, M.A., D.Sc. London: Macmillan and Co., Ltd. 1914.

THE object of the investigations described in this book was to obtain definite information as to the different pigments and mediums used at various dates, by means of which information the dates of works of art could be fixed and forgeries detected. For this purpose the author had to devise some special pieces of apparatus for the removal and examination of microscopical samples. After dealing with the properties and reactions of certain pigments which are of importance in the history of art he passes to the description and identification of the pigments used in the illuminated manuscripts of all nations, and applies the information thus obtained to the examination of pictures, finally showing in tabular form the range in time of the use of the most important pigments, summarising the results from the year 800 to 1800. Mediums are then similarly treated, but possibly the most interesting part of the book is that devoted to the application of microphotography to the study of brush work. This is admirably illustrated by plates which are fully explained, and the author shows how, from a careful study of microphotographs, conclusions may be drawn as to the authenticity of pictures.

Some Fundamental Problems in Chemistry, Old and New. By E. H. LETTS, D.Sc., &c. London: Constable and Co., Ltd. 1914.

THE aim of the author of this book is to contrast old views of atoms and elements with modern conceptions of electrons, and for this purpose he first discusses the views of the ancients regarding the nature of matter, and also describes in detail the development of the atomic theory and the Periodic Law. Many numerical data are given relating to determinations of atomic weights, and much of the information in the first part of the book might be learned from the usual text-books; however, the author has a knack of interesting his reader in what might otherwise be regarded as rather dull details, and often puts forward his facts in a novel way, quoting largely from the original descriptions of discoveries. The second part, beginning with Chapter V., deals with the newer chemistry, and in this part the chief facts and theories of radio activity are discussed. The views and work of Lockyer in inorganic evolution, and of Arrhenius on the origin and decay of worlds, are admirably described, and many students will be glad to be able to get a summary of their truly epoch-making work. The author's treatment of his subject is essentially modern, and he is usually and, on the whole, well up-to-date; he makes no mention, however, of recent work on the nature of X-radiation, nor does he allude to Sir J. J. Thomson's latest pronouncement regarding the unknown substance "X₃."

The Russian Year-book for 1914. Compiled and Edited by HOWARD P. KENNARD, M.D., Assisted by NELLIE PEACOCK. London: Eyre and Spottiswoode, Ltd.

THIS year-book is invaluable for all who are interested in the resources and activities of the Russian Empire, and contains much general information which will be useful to the intending visitor. Many new diagrams have been added, and the statistics have in all cases been brought down to date. An interesting section on Russian literature is now included, giving a short account of its development and chief features.

The Carnegie Trust for the Universities of Scotland. Twelfth Annual Report (for the year 1912-13). Edinburgh: The University Press. 1914.

THE twelfth annual report of the Carnegie Trustees is somewhat more detailed than previous reports, giving a general account of the operations of the trust during the past five years. The report clearly shows how greatly the Trust has fostered and encouraged a spirit of research among University students and others, and testifies to the continued success of the scheme. The main features of the plan of endowment of post graduate study and research are outlined, and annotated lists are given of the published works of beneficiaries.

Annual Report of the Board of Scientific Advice for India for the Year 1912-13. Calcutta: Superintendent Government Printing Office. 1914.

THE chemical work done in the laboratory of the Industrial Section of the Indian Museum at Calcutta during the year 1912-13 was connected almost entirely with the investigation of substances of vegetable origin, fixed volatile oils, tanning materials, drugs, &c. In the agricultural section an important research on the gases of swamp rice soils was begun, and valuable work was done on the date sugar palm. The reports upon the work in geology, botany, zoology, &c., are included in the volume, as well as a short account of the scientific and technical investigations conducted for India at the Imperial Institute during the year ending June 30, 1913.

Bulletin of Armour Institute of Technology, Chicago. Vol. vii., No. 1. Chicago: Armour Institute of Technology Press. 1913.

THIS general information number of the Armour Institute of Technology contains detailed syllabuses of the courses of study at the Institute in the various departments. A complete register of graduates and students, and information relating to fees, scholarships, and prizes are also included. The four-year courses in Mechanical Engineering, Electrical Engineering, Chemical Engineering, &c., appear to provide a well-balanced system of study, and the Institute is doing a useful work in providing all classes of students with opportunities of obtaining a thoroughly scientific technical education.

Albin Haller. By ERNEST LEBON. Paris: Gauthier-Villars. 1913.

THIS book is one of the series "Savants du Jour" edited by M. Lebon, and contains an interesting biography of the famous chemist and a vivid picture of his striking personality. The chief publications of M. Haller, whose scientific activity has been remarkable, are briefly summarised. His articles dealing with organic and physical chemistry are grouped together according to subjects—camphors, phthaleins, alcoholysis, &c.—and an analysis is given of their main features, while a *résumé* is also given of each separate article of importance, with full references to the periodicals in which it is to be found. The whole is excellently arranged, and the editor has had M. Haller's own assistance in classifying the papers and reading the proofs.

Principes et Applications de l'Electrochimie. ("Principles and Applications of Electrochemistry"). By O. DONY-HÉNAULT, H. GALL, and PH. A. GUYE. Paris and Liège: Ch. Béranger. 1914.

THIS comprehensive treatise on electrochemistry is divided into three parts. In the first part the fundamental laws of the science are discussed, the phenomena of osmosis being first thoroughly explained. A clear treatment of the ionic hypothesis and electrolytic dissociation is to be found in this first section. In Part II. the technical applications of electrochemistry are described, including the electrolysis of water, of solutions of halogen and other salts, and of fused salts. The authors have been particularly careful to give a fair view of the electrochemical industry as it stands at present, while pointing out its potentialities and the possibilities of its extension in many directions. Only a very limited amount of space has been given to electro-metallurgical processes, those relating to the manufacture of copper being the only ones which are treated in detail. A chapter is devoted to the electric furnace and products obtained with it, and this forms an introduction to the last section, which consists of an excellent account of the electrical combustion of nitrogen, written by M. Ph. Guye, who has done much pioneer work in the subject.

Higher Manganese Phosphides.—S. Hilpert and Th. Dieckmann.—When manganese is heated with red phosphorus, first to 400° for forty-eight hours and then to 600° for the same time in a sealed exhausted tube, the compound MnP_2 is formed. If this substance is cautiously heated in a current of hydrogen phosphorus distils over, and when the weight is constant the residue consists of the phosphide, MnP . Both these phosphides are ferromagnetic.

Atti della Reale Accademia dei Lincei.
Vol. xxiii. [i.], No. 3, 1914.

Chemical Action of Light. Auto-oxidations.—Giacomo Ciamician and P. Silber.—When a solution of acetic acid was exposed to the action of light for seven months it slowly underwent auto-oxidation and formic acid was formed. Glycollic acid in the same conditions was completely auto-oxidised, the products being carbon dioxide and formaldehyde. Malonic acid is only very little affected by oxygen in the light, while succinic acid is only partially oxidised. Saccharic acid undergoes auto-oxidation even in the dark. Cumarin polymerises, and oleic acid yields dioxy-stearic acid and nonyl and azelaic acids, besides other products. In the dark in presence of oxygen oleic acid only acquires a faintly acid reaction.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvii., No. 4, 1914.

Action of Alkaline Reducing Agents on Disulphoxides and Sulphoxides.—A. Gutmann.—When sodium arsenite acts on disulphoxides the latter give up an atom of oxygen, and sulphinates and mercaptans are formed. This behaviour is a further proof of the fact that the two oxygen atoms in the disulphoxides, $R_2S_2O_2$, differ in their power of reacting. The reaction with potassium cyanide-potassium sulphide is similar. Sulphoxides give no reaction with these alkaline reducing agents.

Hydrofluoric Acid and Fluorsulphonic Acid.—Otto Ruff and Hans Julius Braun.—In the preparation of aqueous hydrofluoric acid from fluorspar and sulphuric acid it is best to use about 90 per cent sulphuric acid. If 95 to 100 per cent is used a yield of about 60 per cent of 95 to 96 per cent HF can be obtained, but not anhydrous acid. In the residues some calcium fluorsulphonate is found besides calcium sulphate and unchanged calcium fluoride. From fuming sulphuric acid and fluorspar fluorsulphonic acid can be obtained, the yields being greater the greater the amount of anhydride in the acid. An acid with 60 per cent of anhydride gives nearly the theoretical yield.

Fluorsulphonic Acid.—Otto Ruff.—Sodium fluorsulphonate can be prepared by heating together sodium chloride and fluorsulphonic acid, and extracting the unchanged chloride by means of alcohol. Fluorsulphonic acid is very stable when the temperature is raised, and even at 900° it does not undergo decomposition. At its boiling-point it can be decomposed by sulphur, giving sulphur dioxide and hydrofluoric acid. The author has investigated the red gas formed on heating potassium bichromate with calcium fluoride and sulphuric acid, but has come to no definite conclusions as to its nature. When potassium permanganate and fluorsulphonic acid are gently warmed together a violet gas is evolved, which explodes when shaken or warmed. It is uncertain whether it contains fluorine as an essential constituent or whether it is simply manganese heptoxide.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, May 5, at 3 o'clock, Prof. W. Bateson will deliver the first of two lectures at the Royal Institution on (1) "Double Flowers"; (2) "The Present State of Evolutionary Theory"; and on Saturday, May 9, Prof. C. J. Patten, of Sheffield University, will begin a course of two lectures on "Bird Migration." The Friday Evening Discourse on May 8 will be delivered by Prof. Karl Pearson on "Albinism in Men and Dogs," and on May 15 by Prof. Frederick Keeble on "Plant Animals: A Study in Symbiosis."

Institute of Chemistry.—Past List: March (1914) Examinations.—Of ten candidates who presented themselves for the Intermediate Examination, nine passed:—A. S. Carlos, B.Sc. (Lond.); C. G. Collins; Miss Gwen Dyer, Nat. Sci. Tripos (Cantab.); F. L. Elliott; H. S. Foster; J. J. Geake; G. Harding; J. W. Sewill, B.A. (Cantab.); and G. T. Shipston. Of fourteen candidates who presented themselves for the Final Examination, eight passed. In the Branch of Organic Chemistry—P. K. Dutt M.A., B.Sc. (Calcutta); J. W. Harris, B.Sc. (Lond.), and E. Mather, B.Sc. (Lond.). In the Branch of the Chemistry (and Microscopy) of Food and Drugs, Fertilisers and Feeding Stuffs, Soils and Water—P. S. Arup; C. Ws. McHugo; F. S. Thurston, B.Sc. (Lond.); J. A. F. Wilkin-son, B.Sc. (Lond.); and F. Wright, B.Sc. (Leeds).

Feed Water Difficulties.—"The problem of suitable feed water, although less serious in New England than in other parts of the country, is still a trouble maker in many plants. The formation of scale and the softening of water are due to the simplest of chemical reactions, and by an analysis of the water a competent chemist can readily predict in advance the proper amounts of suitable chemicals necessary to prevent scale or corrosion, and not only save the company the expense of frequent boring and replacing of tubes, but obviate the necessity of attempting to force heat through the same substance with which many of your steam-lines are insulated. The service of a chemist," said Mr. Carl F. Woods, secretary of the firm of Arthur D. Little, Inc., of Boston, when recently speaking before a group of street railway operators, "would prevent the purchase of a special compound at \$1000 a year which consisted of 97 per cent water and 3 per cent molasses, or obviate the necessity of purchasing a mixture of soda-ash, tannin, and water under a brand name at 8 cents a pound when the principal ingredient can be obtained for 1 cent a pound."

What Determines the Quality of Paper.—After discussing the fundamental properties of paper, such as thickness, strength, stretch, opacity, and other physical and chemical properties entering into the make-up of a sheet of paper, Mr. Arthur D. Little, who is eminently fitted to discuss these questions through his long connection with the paper industry and the wide nature of the consulting practice of the concern of which he is president, continues by saying:—"The number of factors which are concerned with the quality of paper in its multitudinous applications to special uses is so great as to prevent consideration or even enumeration of them all. A paper for wrapping hardware or a card for mounting silver jewellery may seem to possess every desirable property, and yet be worse than useless because of a trace of sulphur. A printing-paper may develop 'whiskers' or clog the type by mineral filler, a coated paper may pick or develop odour, a cigarette-paper may burn badly, a writing-paper may allow the ink to spread because the size has been converted into peptones by over-heating, a filter-paper may fail to hold a fine precipitate or unduly retard the passage of liquid, and so on. Enough has been said to suggest to consumers of paper the complexity of the problems involved in the determination of quality, the importance of paper testing, and the advantages to both maker and consumer of carefully considered and intelligently drawn specifications defining quality as a function of intended use."

Embryo Engineers hear a Lecture on Technical Reports.—"The first thing the Engineer must remember when he is retained is that he stands in a fiduciary relationship to his client. He is retained to furnish a report which is to give facts and data which will form the basis for decision as to the advisability of making an investment. The accuracy of these facts must therefore be unquestioned, and they must include all the available material. Moreover, since the report is usually addressed to non-technical people, the language must be clear and simple. The reader should be assumed to know nothing of the subject, and technical terms should be defined when used for the first time." The above remarks were made by Mr. Arthur D. Little, in a recent lecture before the Chemical Society of the Massachusetts Institute of Technology. A large audience greeted the speaker because of the long and varied experience which he has had in consulting practice as a chemist and engineer. Continuing, Mr. Little emphasised the fact that an engineer's success depends on his ability to influence other men, and that therefore the cultivation of good English was an absolute necessity. "The form of the report is extremely important. Although paper, type, and binding have nothing to do with the subject-matter, they influence the reader's opinion and should be carefully considered. The title-page should be attractive, and the table of contents should be very full. The report proper opens with a statement of the object and scope of the report, the general method of attack, and of obligations incurred in the preparation as to sources of material, &c. The body of the report is usually divided into sections, which are treated as separate units, with a summary after each, and a complete summary after the last one. Diagrams are advisable wherever possible, and at the conclusion an appendix is placed, which contains all original material, results of analyses, photographs, personal letters, copies of newspaper clippings, &c., and a bibliography of the literature of the subject."

Printing and Allied Trades Exhibition.—This Exhibition, to be opened at the Royal Agricultural Hall by the Lord Mayor of London on May 13, 1914, promises to be of exceptional interest. It will be the largest and most representative Exhibition of its kind ever held in any part of the world, every available space in the Great Hall, the Gulbey Hall, King Edward's Hall, and the galleries being occupied with exhibits strictly appertaining to the graphic Arts; new machinery and appliances will be shown, alike interesting to the expert and the general public, in addition to a very fine display of specimens of

printing by all processes, including photogravure. The Exhibition has the support and patronage of the various Societies associated with the Printing and Allied Trades, and practically every firm of repute in the industries represented is co-operating to make this quadrennial Exhibition an unqualified success. The Exhibition will remain open until May 30.

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Royal Society of Arts, 8. (Cantor Lecture). "Some Recent Developments in the Ceramic Industry," by W. Burton, M.A.

— Royal Institution, 5. General Meeting.
Society of Chemical Industry, 8. "Apparatus for the Automatic Measuring and Injection of Chemicals," by the Hon. R. C. Parsons "Jets for Mixing," by O. Nagel. "A Reaction of Tetranitromethane," by W. R. Hodgkinson.

TUESDAY, 5th.—Royal Institution, 3. "Double Flowers," by Prof. W. Bateson, F.R.S.

WEDNESDAY, 6th.—Society of Public Analysts, 8. "Detection of Castor Oil Seeds," by G. D. Lander and J. J. Geake. "Composition of Milk," by H. D. Richmond. "Note on 'Sharps,'" by J. F. Liverseege and G. L. Elsdon. A Simple Form of Fat Extractor will be shown by G. A. Stokes.
— Royal Society of Arts, 8. "Inexpensive Motoring," by A. Ludlow Claydon.

THURSDAY, 7th.—Royal Institution, 3. "The Last Chapter of Greek Philosophy—Plotinus as Philosopher, Religious Teacher, and Mystic," by The Very Rev. W. R. Inge, D.D.

— Royal Society, 4. (Election of Fellows). "Some Calculations in Illustration of Fourier's Theorem," and "The Theory of Long Waves and Bores," by Lord Rayleigh. "Protection from Lightning and the Range of Protection afforded by Lightning Rods," by Sir Joseph Larmor and J. S. B. Larmor. "Flow in Metals subjected to Large Constant Stresses," by E. N. Da C. Andrade. "Properties of Magnetically-shielded Iron as affected by Temperature," by E. Wilson. "Eddy Motion in the Atmosphere," by G. I. Taylor.

— Royal Society of Arts, 4.30. "The Punjab Canal Colonies," by Sir James M. Douie, K.C.S.I.
— Chemical, 8.30. "Researches on Santalin," by J. C. Cain, J. L. Simonsen, and C. Smith. "Nature of Molecular Association—Its Relation to Chemical Combination," by W. E. S. Turner and S. English. "Action of Diastase on Starch Granules," by J. L. Baker and H. F. E. Hulton. "Studies in Substituted Quaternary Azonium Compounds containing an Asymmetric Nitrogen Atom—Part III., Resolution of Phenylmethylbenzylazonium iodide into Optically Active Components," by B. K. Singh. "Contributions to the Chemistry of the Terpenes—Part XVII., The Action of Hypochlorous Acid on Camphene," by G. G. Henderson, J. M. Heilbron, and M. Howie. "Reactions by Trituration," by L. H. Parker. "Reaction between Dilute Acid Solvents and Soil Phosphates," by J. A. Prescott. "Influence of the Dilution of Hydrogen Peroxide on the Velocity of Precipitation of Manganese from Ammoniacal Solutions in presence of Zinc," by A. J. Walker and W. Farmer. "Quinone Ammonium Derivatives—Part III., Dihaloid-, Monoazo-, Bisazo-, Nitro-triazole, Bistriazo-, and Compounds containing an Asymmetric Quinquevalent Nitrogen Atom," by R. Meldola and W. F. Holley. "Additive and Substitutive Derivatives of Mercuric Nitrite with Organic Thio-compounds," by P. C. Ray. "Co-ordination of Antimony Halides with Conjugated Compounds," by E. Vanstone. "Absorption Spectra of various Substances containing Two, Three, and Four Benzene Nuclei," by J. E. Purvis. "Kinetics of the Decomposition of Acyl Derivatives of Phenols by means of Alcohol in presence of Acids and Alkalis," by M. Jones and A. Lapworth.

FRIDAY, 8th.—Royal Institution, 9. "Albinism in Men and Dogs" by Prof. Karl Pearson, F.R.S.

— Physical, 8. "Graphic Treatment of the Rainbow and Cusped Wave-fronts," by W. R. Bower. "Gyrostatic Devices for the Control of Moving Bodies," by J. G. Gray.

SATURDAY, 9th.—Royal Institution, 3. "Bird Migration," by Prof. C. J. Patten, M.A.

— Biochemical Society, 4. (In the Chemical Department, Royal Holloway College, Englefield Green, Surrey).

THE CHEMICAL NEWS

VOL. CIX., No. 2841.

ON METALLIC COLLOIDS AND THEIR BACTERICIDAL PROPERTIES.*

THE HISTORY OF COLLOIDS.

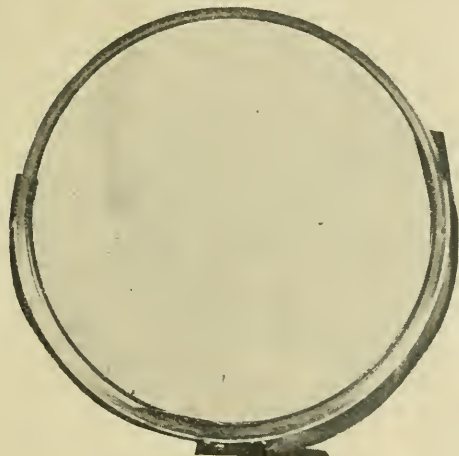
By HENRY CROOKES, F.C.S., A.R.S.M., M.I.E.E.

MAN is always fighting against unseen foes. In the mediæval ages a question was often discussed, viz., "How many angels can stand on the point of a needle?" If instead of angels we say "devils" or "microbes,"—and devils are only angels of opposite polarity—the subject can be brought more clearly to our every day comprehension. Microbes of disease are the "devils" that medical science is always warring against; they are so small as to be invisible to the naked eye, and, in fact, can only be seen

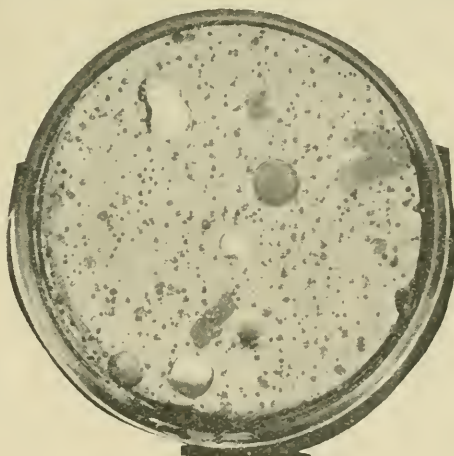
In June, 1903, I exhibited at the Royal Society a number of plate cultures and photographs, illustrating the germicidal action of radium emanations on several forms of microbes. The radium rays undoubtedly kill the microbes, but at the same time, unless administered with the most scrupulous care, they also kill, or *burn up*, the living tissues of the body.

The radium emanations are due to the breaking down of the atom of radium, and electrons are constantly flying off with about two-thirds the speed of light (182,000 miles per second). These electrons are now looked upon as being absolute units of negative electricity. To try and illustrate their size is difficult; imagine one drop of water magnified to the size of the earth (8000 miles diameter); an atom would then be about the size of a walnut or a cricket-ball. Now magnify the cricket-ball or atom to a cube of 100 ft. each side; the electron would be about the size of this dot ($\cdot$) $\frac{1}{1000}$ of 1 in. diameter). The mind cannot conceive such figures.

About that time (1903), or shortly afterwards, the attention of medical men was directed in a critical scientific manner, apart from tradition and empiricism, to the curative effect of certain waters from mineral springs. Laborious research on the part of many workers has revealed the fact that these curative waters contain a number of ex-



I.



II.

PHOTOGRAPHS ILLUSTRATING THE PRESERVATIVE EFFECTS OF "COLLOSOLO ARGENTUM."

Two plates of nutrient gelatin exposed on the window-sill for half-an-hour. No. I. had been covered previously with 'Collosol Argentum' for five minutes, No. II. was untreated; both plates were incubated for forty-eight hours at 20° C. No. I. is sterile, No. II. contains about 350 microbes.—May 20, 1913.

under a high power microscope—about 1000 can be placed on the point of a very fine needle. Modern science has, in spite of their minuteness, found them, identified them, photographed, isolated, cultivated, and finally devised means of killing them. The simplest method of killing microbes is by the application of heat; sunlight has also been found to be a very efficient sterilising agent. Various disinfectants, such as carbolic acid, chloride of lime, permanganate of potash, &c., have been proved to be deadly to microbes. Unfortunately for us human beings, nearly every efficient germicide known until recently has an irritating or destructive action on living organic tissues. The dream of the doctor has been to find an agent that will kill disease, or, in other words, bacteria, and will at the same time do no harm to the tissues of the human body. Immediately following the discovery of radium it was found that the emanations from that wonderful element had a very strong germicidal action, but almost at the same time it was noticed that a very serious burning effect on the skin and flesh was also produced.

Extremely small metallic particles, endowed with continuous, rapid, oscillatory movement known as the "Brownian movement."

This condition under which these particles are present is known as the "colloidal" condition. The word "colloidal" is really a misnomer, but it has gained currency by long use. The actual state in which these particles exist is that of extreme minuteness; they remain in suspension, being kept up by the continuous molecular bombardment of the surrounding liquid. Natural waters contain these metallic particles in comparative small numbers, and the problem arose how to increase the number and thus the efficiency of these particles in a solution. One method, known as Bredig's method, of effecting this result was by using a high tension disruptive electric spark under water, between poles of the metal to be dealt with. Solutions containing an almost incredible number of particles of metal were prepared by these means, and it was soon found that these liquids had a very high germicidal power. After a time it gradually became evident that these electric colloids, as the solutions were called, could not be depended upon; they were not stable and were

* Read before the Royal Society of Medicine, April 8, 1914.

broken down by the presence of electrolytes. The next problem was that of stabilising these colloidal solutions. As the workers increased in number the proposed methods multiplied. Organic compounds of metals were introduced, but all had drawbacks, such as non-stability, irritation, caustic effect, &c.

A few years later, during a research I was engaged in, I noticed a peculiar action of some metals in inhibiting the growth of bacteria in their neighbourhood; as a result of further work in following up this question I exhibited a number of living cultures and photographs of my experiments at the Royal Society and at the Royal Institution in May and June, 1911. The germicidal action of metals in these experiments is, at first sight, very similar to the observed germicidal action of radium, but with this enormous and important difference, that whereas radium kills and destroys the flesh as well as the bacteria, the other metals (in what is now called the colloidal state) kill the bacteria only, and exercise a bland and soothing effect on the animal tissues.

After further work on the subject, entailing about 2000 experiments, I was able to produce a harmless liquid containing metallic particles in suspension, endowed with the above described "Brownian" movement. I have called these preparations "Collosols." The germicidal action of colloid metals in suspension has been known for some time, especially during the last seven or eight years, in connection with medical and therapeutic work; but the great drawback in all previous preparations of this character, as has already been pointed out, is that—(1) They are not stable by themselves; (2) they break down instantly when introduced into a liquid containing even a small proportion of common salt, such as the blood (containing 0.7 per cent salt), and are therefore useless for the human body; (3) they are nearly all irritating to the animal tissues. "Collosols" have none of these drawbacks; they are permanently stable, they do not irritate the tissues, salt does not break them down, and they contain so small a proportion of metal, viz., 1 in 2000, that even a poisonous body like arsenic can be used with impunity. Well-known medical men have stated confidently that the dose is unlimited, as only the bacteria and ferments are killed.

Collosols can be applied topically as a lotion, by intramuscular or intravenous injections, or by the mouth, and from numerous trials made by a large number of medical men, as well as from very many laboratory experiments, it has been proved conclusively that there is no microbe that can withstand the action of collosols, when properly applied, for more than a few minutes.

Silver and Mercury "Collosols" of the normal strength (1 in 2000) were diluted with nine times the quantity of nutrient broth (1 in 20,000), and 10 cc. of this mixture were infected with two loopfuls of a vigorous culture of *B. coli communis*; after shaking, so as to mix thoroughly, streak cultures were made quickly on agar plates, the first within ten seconds, then at two, four, six, eight, and ten minute intervals. These plates were incubated at 37° C. for forty-eight hours, and gave the following results:—

Silver "Collosol" (1 in 20,000) with *B. coli communis*:—
After 10 seconds—Growth.

"	2 minutes	"
"	4 "	"
"	6 "	No growth.
"	8 "	"
"	10 "	"

Mercury "Collosol" (1 in 20,000) with *B. coli communis*:—

After 10 seconds—Growth		
"	2 minutes	No growth.
"	4 "	"
"	6 "	"
"	8 "	"
"	10 "	"

(In each case the blank or control streak gave a vigorous growth).

These experiments were repeated with silver and mercury "Collosols" at the normal strength of 1 part in 2000. In every case *B. coli communis* was killed within ten seconds, the only growth on the agar plates being those of the untreated control streaks. Several comparative tests were made with the *gonococcus* grown on agar plates smeared with fresh blood, with the usual precautions. A plate showing a vigorous growth and answering to the typical tests (that is—Gram-negative, no growth on gelatin or agar at 20° C. without fresh blood, but vigorous growth at 37° C. on agar with fresh blood, and displaying the well-known *diplococcus* in pus cells) was swamped with "Collosol" silver for two minutes, after which time streak cultures were taken and transplanted to agar plates smeared with fresh blood as before, at intervals of two, four, six, eight, and ten minutes, and incubated in the usual way at 37° C. Result—No growth whatever.

I have carried out many series of experiments similar to this; for instance, with a young vigorous growth of *B. tuberculosis*, I found that with "Collosol" Silver (1 in 2000) it was killed in four minutes. With *Staphylococcus pyogenes*, various *Streptococci*, and other pathogenic organisms, I find that all are killed in three or four minutes; in fact, I know of no microbe that is not killed in laboratory experiments in six minutes.

It will be argued that laboratory experiments are not of much value, because of the very different conditions in which bacteria exist in the human body; the answer to this objection is that with a safe bactericide, such as Collosols, of which the dose is unlimited, large quantities, such as one pint or more, can be injected intravenously (this has been done thousands of times with other liquids), and it is well known that a fluid injected into the body soon spreads throughout the whole system. In some circumstances it is desirable and even important to apply colloid metals, not only internally but locally, such as in the case of a diseased joint containing incapsulated bacteria (such as the *gonococcus* or *B. tuberculosis*). I have shown that this can be done by means of a very small electric current of about 30 to 40 milliampères with an E.M.F. of about 50 volts. Two blocks of solid nutrient gelatin were prepared, 2 ins. diameter and 1 in. thick. A current of 35 milliampères was passed through one of these (A) by means of silver pole plates 1½ in. square, covered with flannel soaked in silver collosol; the current, obtained from a medical battery of 24 dry cells, was kept on for twenty minutes, the negative pole being placed on the top. The other block (B) was arranged in exactly the same manner, and left for twenty minutes, but no current was passed. Stab cultures of *B. coli communis* were made vertically through the centre of each block. Three days afterwards I noticed a growth along the line of the stabs, and in order to examine these more closely I made a vertical section of each block close to the stab. I then observed that in block (B) without current there was a vigorous growth of *B. coli* throughout the length of the stab, right up to the surface; whereas, in block (A) with current, there was no growth at the surface, nor for the top eighth of an inch, and below that only a feeble growth for the rest of the line of stab. This proves that the negative current of 35 milliampères had driven the colloidal particles of silver into the gelatin, where they were able to continue their germicidal activity, and that the particles did not soak into the gelatin to any appreciable extent, without the driving action of the electric current.

To show that medical electric currents do not break down collosols, I passed a current of 40 milliampères from the same 24 cells through 10 ozs. of Collosol Argentum contained in a glass vessel for one hour. The same silver pole plates 1½ in. square were used, and were kept about 2 inches apart. After turning off the current the collosol was examined under the ultra-microscope, and it was observed that no change in the "Brownian" movement had taken place.

Much has been said as to the theory of this killing action. How is it brought about? With regard to the

radium emanations it is undoubtedly akin to burning; radium sores are in a way similar to burns but take very much longer to heal. Ultra-violet light, even at the temperature of liquid air (-181°C.) has apparently a disruptive or bursting action. I show photographs illustrating this action.

It seems probable that the action of colloid metallic particles in killing bacteria is due to another cause. Assuming, as seems reasonable, and as has been definitely stated by some writers, that each metallic colloidal particle carries a charge of electricity, these particles in any definite preparation are all electrified in the same manner—negative, for example, in the case of silver—and are therefore mutually repelled, so that in spite of their constant and exceedingly active movement (about 6000 times their own diameter per second), they do not and cannot touch each other, and thus do not lose their charge. If, however, a foreign neutral body (such as a microbe) enters the solution, these electrified particles are not repelled from it automatically, but may even be attracted to it if it happens to carry a charge of the opposite polarity by the action of adsorption; in any case, being of much greater mass, the microbe will receive the charges of many thousands or millions of particles of metal, and this may very conceivably account for its death.

Bacteria are measured under the microscope in terms of μ ($1/1000$ th of a millimetre), and the average size of a coccus may be taken as 1μ diameter, or in the case of bacilli 1μ in length. The size of colloidal metallic particles is, however, very much smaller, and they are measured in terms of $\mu\mu$ ($1/1,000,000$ th of a millimetre). According to Zsigmondy, particles of more than 60 or 70 $\mu\mu$ in a liquid sink to the bottom, while those of less than 3 or 4 $\mu\mu$ cannot be seen under the ultramicroscope, even with bright sunlight as the illuminant. Thus the proportionate size of a microbe and the smallest visible metallic colloid particle is about 330:1, or to give a popular example, their relative sizes are as the elephant in the Natural History Museum compared with the shrew mouse underneath.

The number of colloidal particles in a liquid containing 0.05 grm. of gold per litre, or 0.005 per cent, is, according to Zsigmondy, 1,000,000,000 per cubic millimetre; assuming each particle to be $15\mu\mu$ diameter, owing to the difference in specific gravity, there would be about double the number of particles of silver. As Collosol Argentum contains 0.05 per cent—or ten times the amount of Zsigmondy's typical solution—the number of particles present would be, in round numbers—

$$1,000,000,000 \times 2 \times 10 \times 1000 \text{ per cc.} = 20,000,000,000,000 \text{ per cc. of 15 drops.}$$

An illustration of the protective value of "Collosols" is shown in two photographs (Figs. I. and II.). Two plates of nutrient gelatin peptone, A and B, were exposed on the window-sill for half-an-hour. A had been previously washed with Collosol Argentum, B was untreated. Both plates were then placed in the incubator at 20°C. for forty-eight hours. It will be seen that A is sterile, while B contains about 350 colonies of microbes. It must be admitted that about an equal number of bacteria in the dust will have fallen on the two plates during the time of exposure side by side; the result shows the rôle of colloidal metals in the form of "Collosols" as a protective agent in dressing wounds after operations, and also all smaller scratches, wounds, and sores on the body.

With reference to the medical employment of these preparations, my medical and other friends have, during the past two and a-half years, furnished me with very encouraging reports, which seem to warrant the remedies receiving a more extended trial by the medical profession.

(These preparations are manufactured by Crookes' Collosols, Ltd., and can be obtained at the Company's Laboratory, 109, Ladbroke Grove, London, W.).

SOME ERRORS IN THE DETERMINATION OF THE RARE EARTHS AS HYDROXIDES.

By T. O. SMITH and C. JAMES.

THE writers have observed that when the rare earths are precipitated as the hydroxides and ignited to oxides that the results are higher than when they are precipitated as oxalates and ignited. Moreover, the former method gives results which are not concordant with varying amounts of the precipitant. Since this method has been often recommended for quantitative determinations it seemed desirable that a careful investigation should be carried out.

As a basis for determining the source of error it was thought advisable to compare the following precipitants: Oxalic acid, ammonium oxalate, sodium hydroxide, and ammonium hydroxide. If the cause of error were due to the formation of a basic salt, lanthanum being the most powerful base of the rare earths would tend to give a maximum. It seemed preferable to use lanthanum chloride rather than lanthanum nitrate, since lanthanum hydroxide upon ignition would hold chlorine more readily than nitric acid.

A solution of pure lanthanum chloride was prepared by igniting a very pure lanthanum oxalate, dissolving the resulting oxide in a minimum amount of dilute hydrochloric acid, evaporating to dryness, and taking up in water. The solution was made faintly acid, by a few drops of hydrochloric acid, to convert any traces of basic chloride back to the normal salt.

Oxalic Acid.—Varying amounts of the lanthanum chloride solution were measured out, and precipitated in the cold by the addition of a slight excess of oxalic acid. The volumes in each case were kept constant so as to remove any doubt as to solubility. The precipitated solutions were allowed to stand over night. The oxalate was filtered off, washed with cold water, dried, and ignited. The results follow:—

No.	LaCl ₃ , cc.	Wt. of oxide.	Oxide, per cc.
1 ..	25	0.0866	0.003464
2 ..	25	0.0864	0.003456
3 ..	50	0.1729	0.003458
4 ..	50	0.1732	0.003464
5 ..	50	0.1729	0.003458
6 ..	75	0.2594	0.003459
7 ..	75	0.2596	0.003461
Average			0.003460

Ammonium Oxalate.—In order to avoid the formation of free hydrochloric acid and consequent possible solubility of the oxalate during precipitation, ammonium oxalate was employed as reagent. The operations were identical with the above, except for the substitution of ammonium oxalate for oxalic acid. The results follow:—

No.	LaCl ₃ , cc.	Wt. of oxide.	Oxide, per cc.
1 ..	50	0.1725	0.003450
2 ..	50	0.1726	0.003452
3 ..	25	0.0864	0.003456
4 ..	25	0.0865	0.003460
5 ..	50	0.1729	0.003458
6 ..	50	0.1730	0.003460
7 ..	50	0.1728	0.003456
8 ..	75	0.2594	0.003459
9 ..	75	0.2592	0.003456
Average (omitting 1 and 2) ..			0.003458

Sodium Hydroxide.—Varying amounts of the lanthanum chloride solution were taken, diluted, precipitated at the boiling-point, filtered, washed with hot water, dried, and ignited. The following figures were obtained:—

No.	LaCl ₃ , cc.	Wt. of oxide.	Oxide per cc.
1 ..	25	0.0878	0.003512
2 ..	50	0.1751	0.003502
3 ..	75	0.2619	0.003492

Average 0.003502

The variation of these results with each other suggested precipitation with different amounts of the reagent. Three 50 cc. portions were taken, diluted, and precipitated at the boiling-point with a measured slight excess of sodium hydroxide solution. Three other 50 cc. portions were taken, diluted, heated to boiling, and precipitated with double the amount of sodium hydroxide. The data follow:—

No.	LaCl ₃ , cc.	Wt. of oxide.	Oxide, per cc.
1 ..	50	0.1751	0.003502
2 ..	50	0.1753	0.003506
3 ..	50	0.1755	0.003510

Average 0.003506

4 ..	50	0.1772	0.003544
5 ..	50	0.1771	0.003542
6 ..	50	0.1768	0.003536

Average 0.003541

Ammonium Hydroxide.—Varying amounts of the lanthanum chloride solution were taken, heated to boiling, precipitated with a slight excess of ammonium hydroxide, filtered, washed with hot water, dried, and ignited. The results follow:—

No.	LaCl ₃ , cc.	Wt. of oxide.	Oxide, per cc.
1 ..	25	0.0870	0.003480
2 ..	25	0.0871	0.003484
3 ..	50	0.1740	0.003480
4 ..	50	0.1742	0.003484
5 ..	75	0.2612	0.003483
6 ..	75	0.2616	0.003488

Average 0.003483

When the results of the various precipitants are compared the following facts are brought out:—Ammonium oxalate gives figures similar to oxalic acid, with the exception that when an excess of ammonium oxalate is used the precipitate carries with it some ammonium oxalate. Upon washing the precipitate with water the complex ammonium lanthanum oxalate appears to undergo hydrolysis. When this takes place some lanthanum oxalate is produced in such a fine state of division that it passes through the filter-paper. The first two results among the ammonium oxalate determinations illustrate this fact. It was observed that these filtrates were somewhat opalescent.

The amounts of oxide are high when sodium hydroxide is used. This is evidently not due to the formation of a basic salt, since, when a large amount of sodium hydroxide is used, still higher results are obtained. The above facts indicate the carrying down of sodium. In order to prove the presence of sodium in the oxide it was dissolved in hydrochloric acid, and the solution tested for sodium by means of the flame coloration and the spectroscope. Both gave very decided tests for sodium.

Ammonium hydroxide was substituted for sodium hydroxide because of its volatile nature. But in this case also high results were obtained, although not as high as when sodium hydroxide was used. A qualitative analysis of the lanthanum hydroxide revealed traces of chloride which would indicate the formation of a certain amount of basic chloride. It is highly probable that ammonium hydroxide would give quantitative results if the lanthanum were present as the nitrate, because upon ignition the basic nitrate if formed would be readily broken down to oxide.

Durham, New Hampshire,
Feb. 24, 1914.

ANOMALOUS ROTATORY DISPERSION.*

By Prof. LEO TSCHUGAEFF, Royal University, St. Petersburg.

It has been well known since Biot's classical work on rotatory polarisation that most of the colourless active bodies exhibit "normal" rotatory dispersion, the numerical values of the optical rotation continuously increasing with decreasing wave-length (*cf.* H. Landolt, "Das Optische Drehungsvermögen," II. Aufl., Braunsch., 1898; P. Walden, *Berl. Ber.*, 1905, xxxviii., 345).

The dispersion ratios $\frac{[\alpha]_D}{[\alpha]_C}$ of compounds of this class vary for the most part within the limits 1.8 to 2.0. Quartz, cane sugar, different active hydrocarbons, and alcohols may be cited as examples of such bodies.

Biot was also the first to point out that there are several exceptions to this rule, which belong to the domain of "anomalous" rotatory dispersion. This term is generally applied to those cases in which the optical rotation passes through a maximum or through a zero value, or decreases with decreasing wave-length. The rotation and dispersion of these substances are, however, largely influenced by the temperature and by the nature of the solvent, so that a substance which shows anomalous rotatory dispersion under some conditions may become normal under other conditions.

In the present state of our knowledge we can assume that all the cases of anomalous rotatory dispersion hitherto described may be divided into three classes.

1. To the first class belong all those cases in which anomalous dispersion is due to the *superposition* of the optical rotations of two (or more) *different kinds of normally dispersing molecules* differing in rotatory dispersion as well as in the sign of their rotation.

It was shown by Biot that dispersion of this kind may be observed in mixtures of dextro-rotatory camphor with laevo-rotatory oil of turpentine, and Arndsen put forward the supposition that the anomalous dispersion of tartaric acid is due to the same cause (*Ann. Chem. Phys.*, 1858, [3], liv., 858). Mixtures of l menthone with isomenthone may be cited as a further example (L. Tschugaeff, *Zeit. Phys. Chem.*, 1911, lxxvi., 469).

2. Another type of anomalous rotatory dispersion is intimately related with the existence of *absorption bands* in the spectra of the active compounds in question. The discovery of this type is due to the French physicist, A. Cotton ("Recherches sur l'absorption et la Dispersion de la Lumière par les Milieux doués du Pouvoir Rotatoire," Thèse, Paris, 1896).

Cotton pointed out in 1896 that the dispersion curves of certain coloured solutions, containing, for example, double tartrates of copper or of chromium, go through a maximum in the next neighbourhood of the absorption band, the sign of the rotation being subsequently changed, and the curve going through a second maximum of the opposite sign.

Cotton has shown further that the anomalous dispersion in absorbing bodies is intimately allied with the so-called circular dichroism; that is to say, the two circular rays resulting from the original plane vibration are not equally absorbed by the active body.

It is well to mention here that Drude ("Optik," 1906), to whom we are indebted for a general electronic theory of dispersion, has shown that this theory is quite in accordance with Cotton's experimental results.

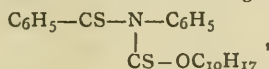
Cotton carried out his remarkable investigation with solutions of complicated composition; he was not able to isolate his active complex salts nor to obtain them in the state of purity. The same is true of the subsequent measurements of McDowell (*Physical Review*, 1905, p. 163) and of Grossmann (*Chem. Centr.*, 1908, ii., 1996; *Zeit. Phys. Chem.*, 1910, lxxii., 93), who repeated and extended Cotton's experiments.

* A Contribution to a General Discussion on "Optical Rotatory Power," held before the Faraday Society, March 27, 1914.

Five years ago I discovered (*Berl. Ber.*, 1909, xlii., 2244) a series of coloured and active compounds showing anomalous rotatory dispersion of the same type as Cotton's double salts. These compounds were derivatives of the menthyl-, bornyl-, and fenchyl-xanthates and of the corresponding thiourethanes.

It was pointed out that there is a general parallelism between the absorption spectra of these bodies and the shape of their dispersion curves (L. Tschugaëff and A. Ogorodnikoff, *Zeit. Phys. Chem.*, 1910, lxxiv., 503; 1912, lxxix., 481). A still closer parallelism holds between the dispersion and absorption produced by one and the same active body in different solvents, the absorption and the dispersion curves being always displaced in the same direction by passing from one solvent (toluene) to another (acetone).

On the other hand, evidence was brought forward that the anomalous dispersion was not due to the influence of the solvent, since the compounds in question showed this property also in a state of superfusion (L. Tschugaëff and A. Ogorodnikoff, *Ann. Chim. Phys.*, 1911, [8], xxii., 137). But still more noteworthy is the recent work of Bruhat (*Comptes Rendus*, 1911, cliii., 248) and Cotton (*Comptes Rendus*, 1911, cliii., 245), who succeeded in observing circular dichroism in one of my substances—I : 2 diphenyl-3-l-bornylimido xanthide—of the following constitution :—



and pointed out that the connection between this phenomenon and the sign of the optical rotation in both the antipodes is exactly the same as is required by theoretical considerations.

During the investigations performed in my laboratory it was shown that abnormalities may occur in the shape of the dispersion curve of an active and colourless compound if it exhibits an ultra-violet absorption band in the neighbourhood of the visible spectrum (L. Tschugaëff, *Zeit. Phys. Chem.*, 1911, lxxvi., 469; *Bull. Soc. Chim.*, 1912, [4], xi., 718; L. Tschugaëff and A. Kirpitchenff, *Bull. Soc. Chim.*, 1913, [4], xiii., 796).

Thus the dispersion ratio $\frac{[\alpha]_F}{[\alpha]_C}$ of many ketones goes far beyond the normal limits mentioned above, e.g. :—

Substance.	$\frac{[\alpha]_F}{[\alpha]_C}$	Solvent.
Camphor	2.69	Methylic alcohol
Epicauphor	2.76	Methylic alcohol
aa-Dibromcamphor	3.13	Benzene
aa-Diiodocamphor	3.41	Benzene
Dihydrocarvone	3.30	None
Pulegone	2.76	None
1-Methyl-cyclohexan-3-one	3.50	None
Nopinone	3.75	None
Pinonic acid	2.63	Methylic alcohol

The dispersion curves of such ketones for the most part cannot be expressed by the simple formula given by Drude—

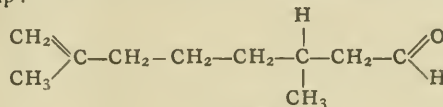
$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2}$$

Moreover, the rotations are influenced very largely by the nature of the solvent, just as is the case in substances showing anomalous rotatory dispersion.

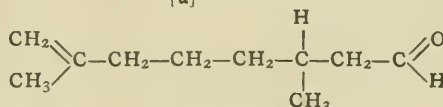
On the other hand, it is well known that the ketones exhibit a general absorption band at about 3500 to 3800 A.U., whereas the saturated hydrocarbons and alcohols are practically diatonic for these radiations. We are therefore justified in concluding that the exaltation of the dispersion ratio $\frac{[\alpha]_F}{[\alpha]_C}$ in the ketones is intimately associated with the nature of the absorption spectra of these compounds.

As a matter of fact, it was shown by Darmon ("Recherches sur la Polarisation Naturelle et la Polarisation Rotatoire Magnétique," Thèse, Paris, 1910) that camphor exhibits the typical form of anomalous dispersion in the neighbourhood of the ultra-violet absorption band.

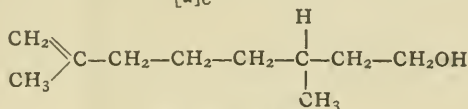
Quite the same seems to be true in the case of aldehydes, which, like the ketones, show selective absorption in the ultra-violet, as was pointed out recently by Henry and others. Miss S. Matthiesen undertook at my suggestion the optical study of the following members of the citronellal group :—



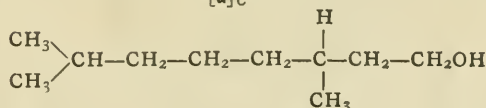
$$\frac{[\alpha]_F}{[\alpha]_C} = 2.42.$$



$$\frac{[\alpha]_F}{[\alpha]_C} = 2.40.$$



$$\frac{[\alpha]_F}{[\alpha]_C} = 2.04.$$



$$\frac{[\alpha]_F}{[\alpha]_C} = 1.93.$$

It will be seen that the aldehydes examined possess almost as high a dispersion as many ketones, whereas the corresponding alcohols give quite normal dispersion ratios. (To be continued).

CHEMICAL REACTIONS AT VERY LOW PRESSURES.*

I.—THE CLEAN-UP OF OXYGEN IN A TUNGSTEN LAMP.

By IRVING LANGMUIR.

ABOUT three years ago we had occasion to measure the amounts of gas given off by a tungsten wire when heated in a vacuum. We were surprised to find that amounts of gas as great as 1000 times the volume of the filament were apparently given off without any indication that the source of supply was nearing exhaustion. Careful investigation showed that the gas really came from the decomposition of the vapour of vaseline used on a stopcock, placed between the vacuum pump and the lamp containing the tungsten wire. The apparatus was therefore reconstructed, avoiding the use of stopcocks, but still the steady evolution of gas was observed when the filament was

* Paper read before the New York Section of the American Chemical Society. From the *Journal of the American Chemical Society*, xxxv. No. 2.

heated, although at a much smaller rate than previously. The source of this gas was found to be water-vapour given off by the glass of the bulb, which, coming into contact with the heated wire, produced hydrogen and oxidised the tungsten. The hydrogen was indicated by the McLeod gauge, whereas the water-vapour had not been. Further study showed that, to avoid such evolution of gases, the bulb must be heated to a temperature of at least 360° for an hour or more, after the lamp has been exhausted with a mercury pump. During this heating of the bulb, it is necessary to absorb the water-vapour with phosphorus pentoxide, or, much better, with liquid air. In order to be able to measure the quantities of gas accurately, we avoided the use of charcoal or any other porous material in connection with liquid air, but depended simply upon the low temperature to condense out water-vapour and carbon dioxide. For this purpose the tube connecting the lamp bulb with the rest of the apparatus was bent in the form of a U, which was kept immersed in liquid air during the whole of the experiment.

When these precautions were taken, it was found that relatively little gas was evolved when the filament was heated. The gas actually obtained from the filament was given off nearly instantaneously when the metal was heated for the first time to a temperature exceeding about 1500° . This gas usually amounts to from three to ten times the volume of the filament, and consists mostly of carbon monoxide. (All volumes of gas given in this paper are supposed to be measured at atmospheric pressure and at room temperature).

It may be of interest to give the results of the analysis of the gas given off from the bulb during the heating to 360° . Before heating the bulb, it was thoroughly dried out at room temperature over liquid air, and the gases obtained in this way were pumped out and rejected. Upon then heating the bulb to 360° for an hour, the gases given off were approximately as follows:—

300 cu. mm. water-vapour,
20 cu. mm. carbon dioxide,
4 cu. mm. nitrogen.

The bulb in this case was an ordinary 40 watt tungsten lamp bulb, made of lead glass. For a description of the method of analysis used, see *Journ. Am. Chem. Soc.* (1912, xxxiv., 1313).

In all of the work described in this paper, pressures were measured by a McLeod gauge, which was capable of measuring accurately to pressures as low as 0.01 micron of mercury (0.00001 mm. of mercury). From the known volume of the system and the pressure in it, we calculated the number of cm. of gas in the system, and the results in general are given in terms of quantity of gas rather than in pressures.

We have very carefully tested out the reliability of the McLeod gauge, and find that for all gases that are not condensed in a vacuum system at the temperature of -78° (solid carbon dioxide and acetone), the McLeod gauge gives extremely accurate results. But this gauge does not correctly indicate the pressure of such easily condensable gases as water-vapour, oil-vapour, or mercury-vapour, nor does it indicate correctly the pressure of any gas in the presence of even small amounts of water-vapour.

During some of the experiments on the evolution of gas from a tungsten wire, we noticed that if the filament was heated at a high temperature in gas which had previously been given off by the filament or obtained in any other way, the pressure would gradually decrease.

This clean-up of gas was known to exist in ordinary commercial tungsten lamps. There are several indications of this. In the first place, it was known that when a tungsten lamp is first lighted, after having been sealed off from the pump, there nearly always occurs a flash of blue glow in the lamp. This gradually becomes less intense, and finally, after flickering a few times, completely disappears. Other indications were obtained by attaching a radiometer to the lamp bulb. If, by swinging the lamp,

the radiometer vanes were set in rotation, the time necessary for them to come to rest was at first only a few minutes. After the lamp had been burning several hours, the time necessary for the radiometer to stop increased to about an hour. Another and more accurate way of indicating this change in pressure is by means of quartz fibre, placed in the lamp bulb, close to the filaments, one end being attached to the glass close to the base of the lamp, and the other end swinging freely in the vacuum. In one typical experiment the pressure had been 0.018 micron, at the moment of sealing the lamp off from the pump. Upon shaking the lamp so that the fibre was set in vibration, and then placing the lamp in a quiet place, it was found that it took sixty-six minutes for the amplitude of the vibrations to become one-half the original amount. After this lamp had been running at 1 w.p.c. for about three hours, the time necessary for the amplitude to decrease 50 per cent had become 115 minutes. In other words, the amount of damping of the filament had decreased in the ratio of 1.75:1. This indicates that the pressure must have been at least as low as 0.010 micron, and presumably very much lower, because even in a perfect vacuum, the filament would probably not have vibrated much longer than 115 minutes to half amplitude.

Evidence of a clean-up of gas in presence of electric discharges is not uncommon. For example, it is well known that in the Moore tube, or in Geissler tubes in general, the vacuum steadily improves. The same observation has repeatedly been made in Röntgen ray tubes. It has been generally assumed that the gas in these cases is driven into the electrodes, or into the glass, or is absorbed by the metal which sputters from the cathode.

In order to gain a clear insight into the nature of the changes occurring in tungsten lamps during life, it was decided to investigate in some detail the causes of the clean-up in such lamps, and to study the behaviour of various gases in this regard.

Clean-up of Hydrogen.

When a tungsten filament is heated above 1300° K in hydrogen, at low pressures, the hydrogen gradually disappears. (In this paper the letter K—Kelvin—will be used to denote absolute temperatures, in accordance with the recommendations of the Association International du Froid; see *Chem. Ztg.*, 1911, xxxv., 3). It has been shown in a previous paper (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 1310) that this action is caused by the hydrogen becoming dissociated into atoms in contact with the filament, the atoms then being driven on to the bulb, and there held by adsorption, or some other cause. The hydrogen on the bulb is in a particularly active form, and is capable of reacting at room temperature with oxygen.

Since these experiments were made, further investigation of the clean-up of hydrogen has been carried on, and interesting results have been obtained. These, however, will be given in a subsequent paper.

Clean-up of Oxygen.

It is well known that metallic tungsten oxidises in the air at a red heat, and becomes covered with a layer of the yellow oxide, WO_3 . At a white heat the oxide volatilises easily, forming a yellowish white smoke.

The first experiments with a heated tungsten filament in oxygen at a very low pressure showed that the oxygen disappeared fairly rapidly, without producing any darkening of the bulb. The rate of disappearance was proportional to the pressure of oxygen, but if the temperature of the filament was above 1500° K the rate did not seem to increase very rapidly with rising temperature. Also, when different lengths of filament were heated in the same bulb, the rate was found not to vary in proportion to the surface of the filament. Further investigation showed that the measured rate was to some extent limited by the rate of diffusion of the gas from the pump bulb and McLeod gauge over into the lamp bulb. At low pressures much

longer times are necessary for the equalisation of pressures than at ordinary pressures.

To avoid this resistance to the flow of the oxygen, several changes were made in the apparatus.

The apparatus used for the final experiment (Exp. 265) is diagrammatically represented in Fig. 1. The lamp bulb B was made large (1020 cc.), so as to have as large a proportion of the oxygen as possible in immediate contact with the filaments. Below the lamp is a tube, L, immersed in liquid air, which serves to exclude mercury vapour from the lamp. The lamp contained three sections of filaments

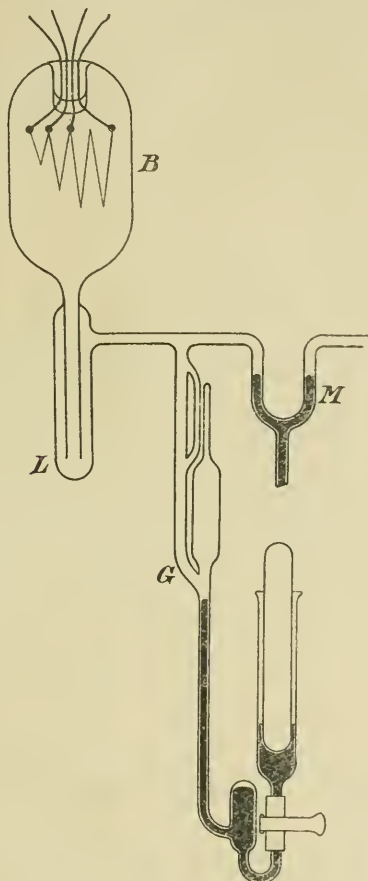


FIG. 1.

with four leading-in wires, so that any one of the sections could be heated to any desired temperature.

The diameter of the wire was 0.0394 mm. The lengths of the sections were:—

Section.	Length (cm.).	Area (sq. cm.).
a	5.4	0.067
b	14.6	0.181
c	47.0	0.583

The tubing between the bulb and the McLeod gauge G was made as short as possible, about 25 cm., and of large diameter (about 0.8 mm.) internal diameter, so that the resistance offered to the flow of gas would be as small as possible. For the same reason the volume of the McLeod gauge was made small (50 cc.). The apparatus was exhausted by a Töpler pump through the mercury seal M, through which also fresh supplies of oxygen were admitted.

After thoroughly exhausting the system (bulb heated one hour at 360°), and freeing from water-vapour and carbon dioxide, a definite amount of pure oxygen was admitted, and the seal M closed. After taking a reading of the gauge the current was suddenly turned on the filament, so as to heat it very rapidly to the desired temperature. Readings of the gauge were taken regularly every minute. With the longest section of filament, especially at the higher temperatures, the oxygen disappeared so rapidly that it was nearly gone in one minute. In these cases the current was turned off after a few seconds, and a reading of the gauge taken. The time intervals were measured by a stop-watch.

When the filament was heated to a temperature between 900° and 1200° K in oxygen, it immediately became coated with an oxide film which was at first straw-coloured, and gradually changed to dark blue and then to a dull brown. Simultaneously, the filament cooled off considerably, and ceased to be even red-hot, so that the current had to be increased considerably to maintain the original temperature. If the temperature was now raised to 1300°, bright spots appeared which gradually extended along the whole filament.* When the filament had become uniform, it was found that the oxide film had entirely disappeared, and that a given current would heat the filament to the same temperature as originally.

The reason for the cooling of the filament is undoubtedly that the oxide is a better radiator of heat than the bright

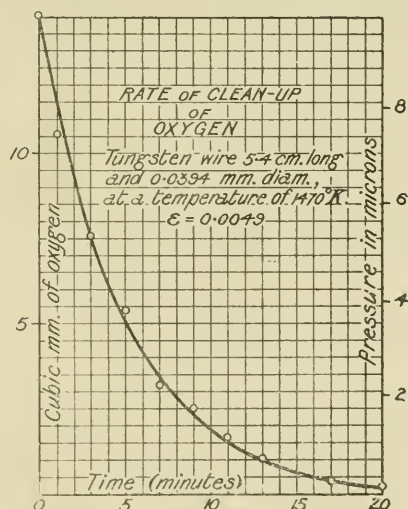


FIG. 2.

metal. The experiment indicates that the oxide volatilises in a vacuum at a temperature of about 1300°. The disappearance of the oxide is not due to dissociation of the oxide, for no evolution of gas occurs when the oxide film disappears.

At temperatures above 1250° the service of the filament always remains bright, even after long treatment in oxygen.

Fig. 2 gives a typical curve showing the way the pressure of oxygen decreases with the time. In this case section a of the filament was heated to 1470°. The ordinates represent the total amount (in cu. mm.) of oxygen gas remaining in the system (bulb, gauge, and tubing). The volume of the system being 1075 cc., 1 cu. mm. of gas corresponds to a pressure of 0.706 micron.

In practically every case the curves obtained were as smooth as this. Sometimes the gas would not completely disappear, but a slight residue, which proved to be nitrogen or carbon monoxide, would remain. In these cases this amount was subtracted from the other readings before

drawing further conclusions from the results. Before admitting fresh oxygen, these residues of foreign gases were always pumped out.

In some of the early experiments it had been found that the rate of clean-up of the oxygen was nearly independent of the temperature of the filament. One of the hypotheses that seemed to account for this was that the observed rate was simply the rate at which the oxygen came into contact with the filament.

It became of interest, therefore, to calculate from the kinetic theory at what rate a gas at low pressures would come in contact with a solid body.

Calculation of Greatest possible Rate of Clean-up.—Let us consider a square centimetre of a surface exposed to the pressure of a gas. According to the kinetic theory, the pressure is caused by the impact of the molecules. Let v be the average velocity with which the molecules strike the surface, and let m be the mass of the molecules which strike a square centimetre of surface per second. Now, according to the laws of mechanics, the force exerted by a series of collisions is equal to the momentum given up to the surface per unit time. Since the molecules leave with the same velocity with which they strike the surface, the momentum given up per second will be $m \times 2v$. This is equal to the pressure, whence—

$$m = p/2v \quad \dots \dots (1).$$

We can thus calculate the mass of gas which comes into contact with each sq. cm. of surface, if we know the pressure and the average velocity of the molecules.

According to the kinetic theory, the mean square velocity $\bar{v}^2$ of the molecules in a gas can be calculated from the equation—

$$p = \frac{1}{3} d \bar{v}^2 \quad \dots \dots (2),$$

where d = density of the gas.

The ordinary gas law $pV = RT$ can be written—

$$p = dRT/M \quad \dots \dots (3),$$

where M = molecular weight.

Combining this with Equation 2, we get—

$$\bar{v} = \sqrt{3RT/M} \quad \dots \dots (4).$$

If we assume that $\bar{v} = v$ then from (1) and (4) we may obtain the approximate formula—

$$m = \sqrt{M/RT} \cdot \frac{p}{\sqrt{3}} \quad \dots \dots (5).$$

Knudson (*Ann. Phys.*, 1908, xxviii., 999), by making use of Maxwell's distribution law, has avoided the above assumption, and has obtained equations which should be rigorously correct. Careful experimental investigations have proved the accuracy of the equation. From Knudson's formulae, the following equation for the value of m is readily obtained,—

$$m = \sqrt{M/RT} \cdot p/\sqrt{2\pi} \quad \dots \dots (6),$$

which gives results 38 per cent larger than the previous formula.

To apply this formula to the case in hand, we place $R = 83.2 \times 10^6$ and for oxygen $M = 32$. For room temperature (25°) T is 298° , whence—

$$m = 14.3 \times 10^{-6} p.$$

Here p is to be expressed in dynes per sq. cm. If we express p in microns of mercury, we have—

$$m = 19.1 \times 10^{-6} p \text{ grms. per sec. per cm.}^2 \quad \dots (7).$$

One cu. mm. of oxygen at room temperature and atmospheric pressure weighs 1.30×10^{-6} grms. Hence the rate at which oxygen, at a pressure of p microns, comes in contact with 1 sq. cm. of surface is $14.6 \times p$ cubic mm. per second per cm.²

Now, in general, not all of the oxygen molecules which strike the filament will combine with it, but only a certain proportion will do so.

Let us represent by ϵ the ratio of the actual rate at which oxygen disappears to the rate which would prevail if the oxygen combined with the filament as fast as it comes into contact with it. Let q be the quantity of oxygen in the system at any time, t . Then we have—

$$dq/dt = \epsilon \times 14.6 pA \quad \dots \dots (8),$$

where q is expressed in cu. mm. at 298° K and atmospheric pressure.

p = pressure in microns of mercury.

A = area of filament in sq. cm.

t = time in seconds.

ϵ = fraction of molecules of oxygen which strike the filament that combine with it.

The quantity of gas q in the system can be readily calculated from the pressure and temperature of the gas and the volume of the system. In the present experiments the volumes of the different parts of the apparatus had been measured. If the lamp bulb is at room temperature we have—

$$q = pv/760,$$

where—

q = quantity of gas in the whole system in cubic mm. at 760 mm. pressure and 25° .

p = pressure in microns.

v = volume of system in cc.

When any part of the apparatus, for example, the lamp bulb, is heated above room temperature, then in calculating v we add the volumes of the various parts at room temperature and then add the product of the lamp volume by the square root of the ratio of the absolute room temperature to the bulb temperature. That is, if the bulb is at 300° (573° abs.), instead of taking its real volume, 1020 cc., we take $1020 \times \sqrt{298/573} = 734$ cc. Knudson explains fully the reason for multiplying by the square root of the temperature ratio (*Ann. Phys.*, 1910, xxxi., 205). We have thoroughly tested out this rule, and find that at pressures below about 10 microns it holds accurately. Let v_0 be the effective volume of the system, as calculated above, then we have—

$$q = pv_0/760 \quad \dots \dots (9).$$

By combining (8) and (9) we obtain—

$$dq/dt = 11,100 \epsilon q A/v_0,$$

whence—

$$\epsilon = 207 \times 10^{-6} \frac{v_0}{At} \log \frac{q_0}{q} \quad \dots \dots (10).$$

Here q_0 is the amount of gas originally present and q is the amount after t seconds. v_0 and A are expressed in cm. units.

Results of Experiments.—Such a large number of experiments were made that it would be impracticable to give anything more than a summary of the results along with a few typical illustrations. A particular study was made of the effect of the following four factors on the rate of clean-up:—

1. Pressure.
2. Length of filament.
3. Temperature of filament.
4. Temperature of bulb.

Previous experiments with smaller bulbs had shown that the oxygen, even at the lowest pressures, combined with the filament to form WO_3 . This was found by determining the loss in weight of a filament during treatment in oxygen and comparing this loss with the amount of oxygen which disappeared. An additional check was had by measuring the increase in the electrical resistance of the filament when cold, and also when heated. The specific resistance and the temperature coefficient of the resistance are not affected by heating in oxygen. From the changes in resistance the change in diameter could be calculated, and was found to agree well with that obtained by direct weighing after breaking open the lamp. In all the experiments the ratio of loss of weight to the weight of oxygen

cleaned up was very close to that calculated from the ratio $W:30$.

Only in rare instances was enough oxide deposited on the bulb to be visible; whereas, if the equivalent amount of tungsten had been on the bulb it would have been nearly black. This is an indication that the oxide must be of very light colour.

It is an interesting fact that when tungsten is heated to a very high temperature in nitrogen which contains traces of oxygen the blue oxide W_2O_5 is formed. In pure oxygen at high or low pressures this oxide never seems to be formed, except when the temperature is so low that the oxide remains on the filament instead of distilling off. This fact would indicate that the yellow trioxide is produced extremely rapidly directly on the filament, while the blue oxide is formed only by subsequent reduction of the trioxide.

All the experiments with oxygen gave results that were easily reproducible. The errors seemed to be only such as would occur from errors in the measurements of the temperature of the filament. In marked contrast with the experiments on the clean-up of hydrogen we never found any indications of fatigue in the clean-up of oxygen.

(To be continued).

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

SAIL FLYING.

Dr. A. Magnan, Director of the Ecole des Hautes Etudes, has just presented to the Congress of the Sociétés Savantes a paper concerning a new apparatus invented by him with a view of enabling men to fly with sails, in the same way as flying birds, by utilising only the force of the wind, excluding all other propulsion whether motive or muscular force. Flying with sails is a sort of continual swooping. The sailing bird does not appear to utilise any acquired speed. It does not appear to descend. Its wings are motionless in all directions. Sea birds especially employ this kind of flight to the almost entire exclusion of any other, but they can only do this with a good deal of wind, and it is when the wind is pretty strong that the most ideal sail-flying is to be observed. Many a time has man tried to imitate sailing birds. But, however, there is only one experimenter worthy of retaining our attention; it is Lilienthal. And in spite of thousands of experiments and trials he was only able, in employing ascending currents—that is to say, by flying against the wind—to cover very small distances. Dr. Magnan has tried fresh experiments of this kind. He has imagined an apparatus copying textually the sea-bird. He has succeeded in this very exactly, thanks to his preceding researches on the relation to the aeroplane with the dimensions that he had found in birds. He has already made some trials with a light apparatus carrying a mannequin, but he has come to the conclusion, like Lilienthal, that if it is important to imagine an ideal apparatus, it is also important to know how to manage it. One must learn how to drive such an apparatus as one learns how to ride a bicycle or to swim. This apparatus calculated for a given weight, including the pilot, has the following dimensions:—

	80 kilos.	90 kilos.	100 kilos.
Alary surface (M^2)	3.52	3.79	4.07
Weight of wings (kilos.)	15.560	17.500	19.450
Spread (metres)	6.02	6.27	6.49
Width of the wing to the middle (metres)	0.75	0.78	0.81
Length of tail (metre)	0.77	0.80	0.83
Weight of tail (kilos.)	3.680	4.140	4.600
Surface of tail (M^2)	0.42	0.46	0.49
Length of apparatus (metres)	2.49	2.59	2.69

M. Magnan has supplied this apparatus with a spread tail so as to copy the example of certain birds who give to the tail and to the wings two contrary incidences, and thus remain motionless for hours together. Moreover, the wings of the apparatus, which are very pointed, have the exact form of the wings of sea-birds. They are also formed like gutters, one-third of the back of the wing being folded downwards at about 60° . M. Magnan, who is well aware of the difficulties that the pilot of such a monoplane must experience in order to realise the sail flying, makes his apparatus public, hoping that some audacious flyer would like himself to attempt to fly against the wind.

THE ELECTROCUTION OF NOXIOUS INSECTS.

A new machine has just been invented by an engineer, M. Friggeri, for the destruction of insects. This electric machine has been tried at Palacios, in the province of Santa-Fé, in the Argentine Republic. The review the *Electricien* explains the machine imagined by M. Friggeri. It is a well-known fact that insects in general, and grasshoppers in particular, are good conductors of electricity. On a carriage that it is easy to transport, M. Friggeri places a spirit motor and a dynamo with an alternating current. At the back of the carriage a drum is placed, on which about 200 metres of insulated cable have been rolled. This cable carries the current to a metallic net or system fixed on to a little vehicle with two wheels, and which carries in its centre a transformer which is destined to raise the tension to 6000 volts and even more. The metallic circuit is disposed on the ground infested with the insects, then the circuit is established between a pole and the dynamo, formed by a stem of iron fixed into the ground and the net. After several trials, which have all been crowned with success, the experiments at Palacios were considered as decisive. Indeed, not only has it been possible to destroy the grasshoppers but also their eggs, which are to be found buried more than 9 centimetres deep in the ground. With the same apparatus provided with a metallic broom worked at the end of an insulated handle, and which is joined to the positive pole of the transformer, it is also possible to completely clean the trees attacked by the *Diaspis pentagona* and other insects.

THE DEATH OF THE EARTH.

A mathematician, M. Veronnet, has just calculated that the living attire of the earth has only two million more years to live. The animals and plants will die. All life will cease progressively on the surface of our globe, and that will happen in less than twenty thousand centuries. And it is the cold that will bring about the death of our planet. This hypothesis has already been mentioned. But this is the first time that learned calculations have assigned such a short existence to terrestrial life. The deductions of M. Veronnet are, however, most rigorous. Two communications concerning them have been made to the Academy of Sciences, but have passed unperceived. M. Veronnet supposes, according to the theory of Helmholtz, that the sun contracts in cooling and constantly loses energy in the form of heat, in proportion to its surface and at the fourth power of its temperature. This is the law of Stefan. In speaking of the actual solar temperature, which is admitted to be of about 6200° , and in making certain hypotheses concerning the state of the condensation of the sun, M. Veronnet finds that the mean actual temperature of the earth must be of about 16° and 34° at the equator. These figures that result from calculations correspond pretty well to the reality. By looking backwards to the past, the learned mathematician perceives that two millions of years ago the sun must have had rays equal to one and a-half of its present rays. The quantity of heat that was dispersed on the earth was much greater than now. In the neighbourhood of the poles at a latitude of 80° the temperature of the surface of the earth must have been

about 90° . So, then, according to M. Veronnet, life could only have appeared from this period and starting from the poles. M. Veronnet has calculated also that in two millions of years the ray of the sun will be reduced by one-tenth. The earth will then be completely frozen, its average temperature being only at 0° . All life will then be impossible on the earth. Death will ensue, preceded probably by a return to a state of barbarity. The duration of life on the earth would thus be of about 4 millions of years, and we would then be actually at about the middle of the curve representing terrestrial life. As for the planet Mars, the same calculations indicate that it has long since been frozen, and that there is no more life on its surface. The speculations of M. Veronnet were the subject of a very interesting discussion at the last sitting of the Société Astronomique de France. M. Camille Flammarion accepts the hypothesis of M. Veronnet only with very great reserve. For him, geology takes the terrestrial life back more than twenty thousand centuries. Then, again, the planet Mars does not seem to him to be a frozen world. Another factor must also intervene in these calculations, according to M. Belot. This is the radio-active properties of bodies. The physicists have shown that the quantity of heat thrown off by radio-active bodies is so intense that the globe would be heated instead of being cooled if the terrestrial mantle contained, as far as a depth of 70 kilometres, the same proportion of radio-active elements as the rocks of the surface. But M. Ponsieux, Member of the Institute and Astronomer of the Paris Observatory, owns that physicists cannot know how radium acts at the formidable pressures that correspond to a depth of 70 kilometres. The rôle of radium in nature is not yet demonstrated. Radiating matter has not yet intervened in laboratory experiments.

A NEW METHOD OF ANALYSIS.

A very ingenious method of analysis, enabling the estimation of substances susceptible of being precipitated in liquids, has just been imagined by M. Dienert, head of the water service of the City of Paris. He has combined the colorimetric process of Dubosq with the projection lantern. By looking in the half of the field of a telescope or lunette at a liquid containing matters in suspension, through a luminous cone, and in the other half of the field at a standard liquid, it is easy to see if the two liquids have the same coloration. By means of a colorimetric scale composed of standard liquids containing determined quantities of matters in suspension it is then very easy to compute, or at least to have a good idea of, the quantity of precipitate contained in a liquid. This same method can be utilised for determining the abundance of microbes in a vaccine or in any liquid, microbes being solids in suspension. M. Dienert applies this method to the estimation of matters contained in spring water, to the standardising of sulphuric acid, &c. The exactness obtained is as great as is the case with quantitative analyses. From 20 to 50 cc. of water are sufficient to make an analysis.

PHOSPHORESCENT CALCITES.

M. Lacroix, Professor at the Paris Natural History Museum, has presented before the Academy a very interesting paper by M. Pisani, who has remarked that certain crystals of carbonate of lime can, under the influence of heat, acquire a remarkable phosphorescence which renders them luminous in the dark. Up till now it was thought that this phosphorescence was due to the presence of small traces of rare bodies. In the most part of calcites there are to be found, indeed, extremely small quantities of yttria; but M. Pisani has operated on absolutely pure crystals of carbonate of lime, and he has observed that when they are heated they become phosphorescent. This curious property of the crystals of carbonate of lime is, then, not due to the presence of rare elements.

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION.

Annual Meeting, May 1, 1914.

The DUKE OF NORTHUMBERLAND, K.G., President,
in the Chair.

THE Annual Report of the Committee of Visitors for the year 1913, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The Report of the Davy Faraday Research Laboratory Committee was read. Thirty three new Members were elected in 1913. Sixty-three Lectures and Nineteen Evening Discourses were delivered in 1913. The books and pamphlets presented amounted to about 289 volumes, making with 710 volumes (including periodicals bound) purchased by the Managers, a total of 999 volumes added to the Library in the year. Thanks were voted to the President, Treasurer, and Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year. The following gentlemen were unanimously elected as Officers for the ensuing year:—

President—The Duke of Northumberland.

Treasurer—Sir James Crichton-Browne.

Secretary—Alexander Siemens.

Managers—The Right Hon. Lord Blyth, Dr. Horace T. Brown, J. H. Balfour Browne, Charles Hawksley, Major Edmund H. Hills, Dr. Donald William Charles Hood, Sir Edwin Ray Lankester, Sir Alexander Mackenzie, Robert Mond, the Right Hon. Lord Moulton, Edward Pollock, Sir James Reid, Bart., the Right Hon. the Marquis of Salisbury, Alan A. Campbell Swinton, and Harold Swithinbank.

Visitors—William R. Bousfield, Charles John P. Cave, Rev. Edward S. Dewick, Dr. William J. Gow, William A. T. Hallows, John W. Jarvis, James Y. Johnson, H. R. Kempe, Dr. Adolph Liebmman, Carl E. Melchers, Dr. H. Forster Morley, Dr. F. W. Passmore, Charles E. S. Phillips, and Arthur J. Walter.

NOTICES OF BOOKS.

A Text-Book of Organic Chemistry. By A. F. HOLLEMAN, Ph.D., F.R.A.Amst. Edited by A. JAMIESON WALKER, Ph.D. (Heidelberg), B.A. and OWEN E. MOTT, Ph.D. (Heidelberg). Fourth English Edition.

A Laboratory Manual of Organic Chemistry for Beginners. By A. F. HOLLEMAN, Ph.D., F.R.A.Amst. Edited by A. JAMIESON WALKER, Ph.D. (Heidelberg), B.A. Second Edition.

New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1914.

WHEN the first English edition of this work was issued ten years ago it was at once recognised by all who are interested in the teaching of organic chemistry to college students as a novel and valuable work, and it took a position in the front rank of text-books from which it has never been displaced. It is no exaggeration to say that its merits have been recognised all over the civilised world, for the original Dutch has been translated into seven languages, in many of which it has passed through several editions; thus there is clearly no need to enlarge upon its special features. In the latest edition much new matter has been added, and more attention has been paid to the application of physico-chemical methods in organic chemistry. The section on tautomerism has been rewritten. The laboratory manual, which is issued in a separate volume, is an appendix to the text-book, and describes the experimental work which can suitably be performed either by students who are using the text-book

or as lecture table experiments. The order of the text-book is adhered to in it, and references are given to the paragraphs of the fourth edition.

Sugar Analysis By FERDINAND G. WIECHMANN, Ph.D. Third Edition. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1914.

In the third edition of this work the material has been cast into a new form, which the author hopes will render it most conveniently accessible in the several branches of the sugar industry. The first part deals with the analysis of sugar and of the materials used in its production, while in the latter part the analytical methods used in the control of cane and beet sugar manufacture and refining are treated in detail. Methods of calculating results are described fully with illustrative examples, in which, however, the author is not always careful to make it clear what units he is employing, as for example in the statement "Volume of metal = 5.0." The book contains a short résumé of the work of the International Commission for Uniform Methods of Sugar Analysis, down to the 7th Session held in New York in September, 1912.

Fuel. By J. S. S. BRAME, F.C.S. London: Edward Arnold. 1914.

THIS book has been written chiefly for engineering students and engineers, and treats of fuel especially from the point of view of power production. Solid, liquid, and gaseous fuels are included, and a section is added on the analysis and calorimetry of fuels; in these chapters only the comparatively simple determinations usually required in commercial work are described. Of the solid fuels coal is naturally treated in the greatest detail, and all available data concerning the composition of the coals of the British Empire have been brought together. Among the liquid fuels a good deal of attention is paid to alcohol, the use of which will in all probability be greatly extended in the near future. The diagrams inserted to illustrate various processes are unusually clear, and the book is admirably adapted for the use of the technical man who needs a good general knowledge of the subject.

The Association of Teachers of Domestic Subjects. Annual Report, 1913.

THIS annual report for the year 1913 contains details of the conferences held by the various branches of the Association during the year and the reports of the committees. From a scientific point of view the chief interest of the report lies in the answers to various questions submitted by members. These questions relate to som incompletely investigated or disputed practical problems in laundry work, cookery, &c., and an endeavour has been made to provide the correct scientific answers to them.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 11, March 16, 1914.

Syntheses by means of Sodamide. Preparation of Higher Homologues of Mono and Dimethyl Camphors and Corresponding Camphols.—A. Haller and Jean Louvrier.—By means of sodamide the monoalkyl and di-alkyl derivatives of camphor, both the symmetrical and asymmetrical compounds, and of camphol, can be prepared. The substituting power of the aliphatic radicles diminishes as one rises in the series. Only the mono-alkyl camphors give rise to oximes. The rotatory power

of the monoalkyl derivatives increases with the molecular weight.

Direct Hydrogenation by Catalysis of Diaryl Acetones and Aryl Alcohols: Preparation of Polyaryl Hydrocarbons.—Paul Sabatier and M. Murat.—The diaryl acetones, benzophenone and its homologues, can be converted by direct hydrogenation over nickel into the corresponding diaryl hydrocarbons. Thus diphenylmethane is formed from benzophenone at about 300°. Similarly, the direct hydrogenation of aryl or polyaryl alcohols at 350° gives rise to the corresponding aryl or polyaryl hydrocarbons, according to the equation $RR'R''\cdot COH + H_2 = RR'R''\cdot CH + H_2O$, where R is an aryl residue and R' and R'' are aryl or formic residues or hydrogen.

Ferrous and Chromous Metaphosphates.—A. Colani.—Ferrous metaphosphate can be prepared by acting on metaphosphoric acid with ferrous chloride or oxalate in a current of carbon dioxide. Ferrous phosphate, obtained by precipitating a ferrous salt with sodium phosphate, washing and drying in air, and then reducing with hydrogen, can be used as the ferrous salt. Ferrous metaphosphate, $Fe(PO_3)_2$, is a white powder very slightly greenish when in large quantities, insoluble in hydrochloric and nitric acids. Sulphurous acid attacks it very readily, sulphurous anhydride being liberated. All attempts to prepare chromous metaphosphate led to the formation of the chromic salt, $Cr(PO_3)_3$.

No. 12, March 23, 1914.

Syntheses by means of Sodamide. Preparation of Allyl Ketones derived from Alkyl Acetophenones and Pinacoline.—A. Haller and Ed. Bauer.—The authors described the preparation of allyl ketones, such as methyl ethyl allyl acetophenone, by preparing the sodium derivative of methyl ethyl acetophenone by means of sodamide, and then treating with allyl iodide. Allyl derivatives of benzylacetophenone can be prepared similarly, and pinacolin very readily gives allyl derivatives when its sodium derivative is treated with allyl iodide.

Use of Manganous Oxide for Catalysis of Acids. Preparation of Fatty and Aryl Acetones.—Paul Sabatier and A. Mailhe.—Manganese oxide, MnO , is an excellent catalyst for acids; it possesses the advantage of being cheap and it can be kept almost indefinitely. It can be used for the preparation of symmetrical or mixed acetones, and also to reduce the acids to give aldehydes. It is obtained by heating commercial precipitated manganous carbonate to 400° in methanol vapour in the catalysis tube, through which the vapours of the acid or mixtures of acids are led. The temperature is kept at 400° to 450°, and if the layer of oxide is 60 cm. long the acids are totally destroyed.

Potassium Tetroxide.—R. de Forcrand.—To prepare potassium tetroxide Vernon Harcourt's method was adopted. The metal is heated in a glass flask to 180° to 200° in a current of pure dry nitrogen, which is gradually replaced by air and then by oxygen. All traces of moisture must be avoided. A yellow deposit, K_2O_4 , is thus obtained. The following values have been found when it is dissolved in very dilute sulphuric acid in a calorimeter:— K_2 sol. + O_4 gas = K_2O_4 sol. + 133.74 cal., K_2O sol. + O_3 gas = K_2O_4 sol. + 46.94 cal. These numbers are both lower than those given by caesium. As the atomic weight of the metal increases the heat of formation of the protoxide diminishes, but the heat of superoxidation (M_2O to M_2O_4) increases.

Density and Atomic Mass of Neon.—A. Leduc.—The author has found that the atomic mass of neon is exactly twenty times that of hydrogen, and hence = 20.15 for $O = 16$, and not 20.0 as stated by the International Commission. Aston (*Nature*, November 6, 1913) has stated that neon can be separated by diffusion into two gases, the densities of which correspond to the atomic

weights 19.9 and 22.1 respectively. The author suggests that the first gas is a mixture of neon and helium, and the second contains a large proportion of nitrogen.

Determination of Traces of Arsenic of the Order of a Thousandth of a Milligramme.—L. Moreau and E. Vinet.—The method depends upon the reaction $12\text{AgNO}_3 + 2\text{AsH}_3 + \text{H}_2\text{O} = 12\text{HNO}_3 + \text{As}_2\text{O}_3 + 12\text{Ag}$. The metal is deposited in the form of a ring. The apparatus consists of—(i.) a hydrogen generating flask; (ii.) a U-tube containing silver nitrate to wash the gas; (iii.) a U-tube containing the liquid to be investigated; (iv.) a small tube bent twice at right angles and containing an acetified solution of N/10 silver nitrate, at the bottom of which the ring is formed. The arsenic is determined by comparing the ring with that obtained with known quantities of arsenic in exactly the same experimental conditions.

Absorption of Carbon Dioxide from the Air by Chromium Hydrate.—Mil. Z. Iovitchich.—Chemically pure chromium hydrate was exposed to the air for five or six days at 25° and the product was then analysed. It was found that its composition agreed with the formula $\text{Cr}_2(\text{OH})_5 \cdot \text{CO}_3 + 8\text{H}_2\text{O}$. This monocarbonate has a constant composition even at 100°. When dried to constant weight at this temperature it retains almost all its carbon dioxide.

Constitution of Potassium Carbonyl.—A. Joannis.—Potassium carbonyl deflagrates in presence of air or water, or when heated. The action of water upon it can, however, be studied by attacking it with water vapour at a tension of some millimetres, or by suspending it in liquid ammonia, and then adding water drop by drop, diluted with liquid ammonia. If the reaction is allowed to proceed slowly no explosions occur. A reddish yellow liquid is thus obtained, and from it glycollic acid can be separated. The reaction is $\text{KCO} \cdot \text{COK} + 2\text{H}_2\text{O} = \text{CH}_2\text{OH} \cdot \text{COOK} + \text{KOH}$.

Hydrates of Primary Amines.—Félix Bidet.—Normal amylamine, isoamylamine, and isobutylamine combine in the cold with the water vapour of the atmosphere, giving crystalline hydrates. In the case of isoamylamine the formula of the hydrate is $\text{C}_5\text{H}_{11}\text{NH}_2 \cdot 2\text{H}_2\text{O}$. All the hydrates melt below 100°, and are remarkable for their high vapour tension, even below their melting-points.

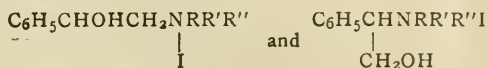
Bulletin de la Société Chimique de France.

Vol. xv., No. 5, 1914.

Rôle of Fluorine in the Animal Tissues.—Armand Gautier.—In the muscles, glands, nervous tissues, blood, and in the assimilating or nutritive secretions of the animal, fluorine is combined with phosphorus and the nitrogenous organic matter. One part of fluorine fixes 350 to 750 parts of phosphorus to the organic matter. In the bones, cartilage, tendons, elastic tissue fluorine is associated with 130 to 180 times its weight of phosphorus. Finally, in the nails, hair, feathers, epidermis, &c., the fluorine and phosphorus are present in the ratios in which they are found in minerals, especially in apatites.

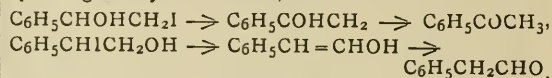
No. 6, 1914.

Determination of the Constitution of Iodohydrines by the Action of Tertiary Amines.—MM. Tiffeneau and Fournéau.—When the two iodohydrines of phenyl glycol, $\text{C}_6\text{H}_5\text{CHOHCH}_2\text{I}$ and $\text{C}_6\text{H}_5\text{CHICH}_2\text{OH}$, are treated with tertiary amines two different reactions take place. In the one case, addition pure and simple occurs with formation for each iodohydrine of an iodohydrate of choline,—



In the other case, elimination of HI takes place, but the hydrogen does not come from the hydroxyl group, and the

result is a vinylic alcohol which isomerises to the corresponding aldehyde or ketone,—



Thus the action of tertiary amines gives a double indication of the structure of iodohydrines; in the first place, aldehydes or ketones are formed in which the oxygen is present in the place occupied by it in the iodohydrine, and, secondly, a salt of choline is formed in which the nitrogen is situated in the place of the iodine. With the primary iodohydrine of styrolene the elimination of hydrazid is the preponderating reaction, while with the secondary iodohydrine the addition reaction is the most important.

Transformation of Limonene into Carvomenthene and Menthane.—G. Vavon.—If limonene is shaken in an atmosphere of hydrogen in presence of platinum black the gas is rapidly absorbed, and all the limonene is transformed into menthane, $\text{C}_{10}\text{H}_{20}$. (The reaction takes place at the ordinary temperature and under atmospheric pressure). But without modifying the experimental conditions it is possible to hydrogenate the exterior double bond, and to prepare carvomenthene; it is only necessary to stop the reaction when 22.4 litres of hydrogen have been absorbed per molecule of limonene.

Action of Diazo Derivatives on Vegetable Oils.—P. Sisley and M. Frehse.—The salts of diazobenzene and of diazonaphthalene do not give colorations with vegetable oils, but the chloride of diazoparanitrobenzene gives very marked and stable colorations in many cases. If the reaction is negative (as with olive oil) the oil turns yellowish orange, owing to the formation of a little phenyl-nitrosamine and decomposition products of the diazoic salt. The colours obtained by different oils do not differ much in shade, being generally red or reddish brown, but since olive oil gives no reaction the purity of a specimen may be determined by means of the test.

MEETINGS FOR THE WEEK.

- MONDAY, 11th.—Royal Society of Arts, 8. (Cantor Lecture). "Some Recent Developments in the Ceramic Industry," by W. Burton, M.A.
- Royal Institution, 3. "The Last Chapter of Greek Philosophy—Plotinus as Philosopher, Religious Teacher, and Mystic," by The Very Rev. W. R. Inge, D.D.
- TUESDAY, 12th.—Royal Institution, 3. "The Present State of Evolutionary Theory," by Prof. W. Bateson, F.R.S.
- Royal Society of Arts, 4.30. (Cobb Lecture). "The Singing of Songs, Old and New," by H. Plunket Greene.
- WEDNESDAY, 13th.—Royal Society of Arts, 8. "Glass Painting in Mediaeval and Renaissance Times," by John A. Knowles.
- THURSDAY, 14th.—Royal Institution, 3. "Identity of Laws, in General and Biological Chemistry," by Prof. Svante Arrhenius, D.Sc., &c.
- Royal Society. "Various Inclinations of the Electrical Axis of the Human Heart—Part I. a. The Normal Heart. Effects of Respiration," by A. D. Waller. "Fossil Plants showing Structure from the Base of the Waverley Shale of Kentucky" by D. H. Scott and E. C. Jeffrey. "Controlling Influence of Carbon Dioxide in the Maturation, Dormancy, and Germination of Seeds," by F. Kidd. "Cultivation of Human Tumour Tissues *in vitro*," by D. and G. J. Thomson. "Nutritive Conditions Determining the Growth of certain Freshwater and Soil Protista," by H. G. Thornton and G. Smith.
- Society of Dyers and Colourists, 8. "Chemistry of Starch and its Transformations," by W. A. Davis. "Analysis of Malt Extracts," by W. P. Drear. "Temperature and Concentration as Affecting Hydration and Soda Absorption during the Process of Formation of Cellulose Monofils," by Clayton Beadle and H. P. Stevens.
- FRIDAY, 15th.—Royal Institution, 9. "Plant Animals, a Study in Symbiosis," by Prof. F. Keeble, F.R.S.
- SATURDAY, 16th.—Royal Institution, 3. "Bird Migration," by Prof. C. J. Patten, M.A.

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CHABANEAU: AN EARLY WORKER ON PLATINUM.

By Prof. JAS. LEWIS HOWE.

Nor long since M. Louis Quennessen of Paris (head of the old house of Des Moutis and Co., platinum refiners) directed my attention to an early worker on platinum, Pierre-François Chabaneau, whose name has so far escaped the historians of chemistry that I think it is not even mentioned in any English or German work, and has only appeared in the last edition of Moissan's "Traité de Chimie Minérale." More recently, through the courtesy of M. Quennessen, I have received a copy of an all but unknown memoir, "Notice sur Chabaneau, Chimiste Périgourdin," par M. Jules Delanoue, printed at Périgueux in 1862, portions of which appear to be of sufficient interest to put on record. This biographical sketch was written in 1857, though not published till five years later, and has for its purpose "to call to the attention of our citizens the useful work, too little known, of a modest man, who unquestionably deserves the first place among the distinguished men whom Périgord has given to the world."

It may be noted that Périgueux is the capital of the old province of Périgord (now in part Dordogne) in south-west France, and has an interesting history going back to the time when it was the old Gallic town of Vesunna, the capital of the Petrocorii. Numerous remains of Vesunna are still in existence, especially baths, temples, an aqueduct, and fragments of the amphitheatre, mostly dating from its Roman occupation. The most notable building of Périgueux is the cathedral of St. Front, belonging to the Byzantine period, which bears quite a close resemblance to St. Mark's at Venice. The town has undergone many vicissitudes, having been taken by the barbarians in the fourth century, the Saracens in the eighth, the Normans in the ninth, the English in the fourteenth, and later restored to the French. It was a stronghold of the Calvinists in the Huguenot wars, and at this time was nearly laid in ruins. In the midst of an agricultural region, it is perhaps best known for its truffes and chestnut fed hogs, the latter being used in hunting for the former.

The early history of Chabaneau is a not unfamiliar one of precocity and hardship.

Pierre-François Chabaneau was born at Nontron (in north-western Dordogne) April 21, 1754. His family were respectable artisans, and he would undoubtedly have followed the obscure career of his parents had not his intelligence and pronounced love of study attracted the attention of his uncle, a monk of the order of St. Antony, at Aveyron (in south-central France, a hundred or so miles from Nontron). Young Chabaneau spent several years with this uncle, pursuing his studies along ecclesiastical lines, destined for the church. He was then sent to Paris for further theological study with the Oratorians, for his uncle was evidently by no means an ascetic. Here, for the sake of his kinsman, he entered upon his studies with great ardour and made such rapid progress that he astonished his teachers; his theses were the admiration of all. Nevertheless, in spite of his brilliant successes, other influences were working on him, as is so often the case with such natures. He was not born for metaphysical studies; his inquiring disposition could not accommodate itself to the abstractions of scholastic philosophy. The unsupported scaffolding of theological hypotheses, the interminable verbiage, the halting arguments of the doctors, all

failed to satisfy the spirit of the young Chabaneau and to accord with his ideas. He demanded mathematical arguments, the definiteness of figures, exact science, and not the science of paradoxes; his reason rebelled at the false ideas they sought to each him. In his dissertations he refuted his teachers by arguments which they could not controvert, and did it so thoroughly that the furious professors finally expelled their audacious scholar, as a punishment for his independence and for his success.

Behold now our young man in the streets of Paris, in the midst of the immense Babylon, without relatives, without friends, having neither experience of the world nor yet money! The six livres, which represented his whole fortune, had been expended in the purchase of a perruque, imperiously demanded by the customs of the times. He dared not return to his angry uncle, nor indeed had he the means for the journey. A kind Providence directed him to the abbé La Rose, to whom he related his story and revealed the extreme embarrassment in which he found himself. The worthy abbé was greatly interested and offered to place him as professor of mathematics in the Jesuit college at Passy (just out of Paris), of which he was the director. The young theologian, whose studies had been confined to Greek, Latin, and philosophy, was absolutely unacquainted even with arithmetic. He was greatly disappointed when he learned what his employment would be, but necessity compelled him to seize even this plank of safety; it was this or nothing. He unhesitatingly accepted the position, without venturing to acknowledge his complete ignorance of the subject he was to teach; he thought that perhaps by work and perseverance he might be able to fulfil his duties. He gave proof on this occasion of energy rare in one of his age, for he was only seventeen.

It is related of Jacques Amyot, the celebrated translator of Plutarch, that while he was a college servant he was possessed of such a desire for knowledge that he studied at night by the light of the fire. Young Chabaneau, whom chance and want compelled to teach others what he did not know himself, and who had great ambition to worthily carry out his task, passed the nights in preparation of the lessons for the following day. He hid his lamp, and then, when all the college world slept, lit it and worked till day. And so it was that, with indefatigable labour, aided by a powerful physical constitution, he made himself master of arithmetic, algebra, and geometry. Nor did he stop with these studies; the passion for knowledge dominated him. He studied experimental physics, natural history, and chemistry, that prodigious science which had just begun to give promise of the astounding wonders which have been realised in our day.

Just at this time was beginning the most active period in the work of Lavoisier, and it was the year before that he had presented to the Académie des Sciences his refutation of the supposed transformation of water into earth, in which the balance was used as an instrument of chemical research, and which soon led to the conception of the permanence of matter, and later to the overthrow of the phlogiston theory. This work of Lavoisier could not fail to make a great impression upon such a mind as that of Chabaneau.

His pupils made rapid progress; they wondered at the knowledge of the young professor, and the director, abbé La Rose, did not cease from expressing his satisfaction.

Chabaneau was now about twenty years old, an age when is often born the love of independence. He knew that the knowledge which he now possessed would suffice to supply all his material needs. He therefore resigned from his position in the college of Passy, after having expressed his most sincere thanks to his benefactor, and, taking lodgings in the Rue des Mathurins, within the city, opened after the fashion of that day a course of public lectures, which met with great success.

Among the most assiduous of his auditors were the young sons of the Comte de Pena-Florida, whose father

had sent them to France to complete their education, and also to procure several professors for a great college for the nobility which he proposed founding at Bergara.

Bergara was a small city in the Basque province of Guipúzcoa in northern Spain, and near the Bay of Biscay. It afterwards came into some prominence as the place where the treaty was signed in 1839 between Spain and the Carlists of the Basque provinces. Of the subsequent history of the college I have been able to learn nothing.

The young nobles gained the affection of their professor and made him the most brilliant offers if he would accept the direction of the college founded by their father. For a long time Chabaneau resisted, but, finally yielding to the earnest solicitation of the young marquesses and other friends, he decided to exchange France for Spain. He immediately began the study of the Spanish language, and with such ardour that in a few months he felt that he had fully mastered it.

He remained three years at Bergara, devoted himself without relaxation to scientific study, and acquired such a reputation that the king, Charles III., wishing to locate him in Madrid, created for him a public Chair of Mineralogy, Physics, and Chemistry, lodged him in one of his palaces, and granted him an annual stipend of 2200 piastres (2400 dols.), a very considerable sum for that time.

The inauguration of his course took place in the presence of the king and all the court. This opening lecture had for its subject the utility and the future of science, and was so remarkable that a Spanish poet composed for the occasion an ode, dedicated to the learned professor. Impelled by the love of science, and wishing to justify the high favour in which he was held by the king, Chabaneau continued with great earnestness his scientific work. As he desired to enter into relations with all the learned men of Europe and to profit by their work, he recognised the necessity of studying English, Italian, German, &c. So energetic was he in his language study that at the age of twenty-five he was master of no less than eight languages, living or dead.

Charles III. provided Chabaneau with a valuable library and a laboratory, considered at that day "magnificent." All the spare moments remaining from his public instruction were devoted to the study of physics, and especially of chemistry. At this period Spanish America was sending to the mint at Madrid not only ingots of gold and silver, but also from time to time a mineral in the form of little white metallic grains, infusible and very heavy. The miners found it associated with gold and with diamonds (?) and called it *platina*, from its similarity to silver (*plata* in Spanish).

The government had no use for the platina, and, fearing it might be used to debase the coinage, ordered (ineffectually) that it should be buried when extracted from the ore. Meanwhile, in 1741, an Englishman named Wood gave the knowledge of platina to Europe; in 1750 Watson announced that it contained a metal hitherto unknown; in 1752 Sheffer, director of the Stockholm mint, and in 1754 Lewis, in London, dispelled all doubt regarding the fact that a new metal actually existed. Baron von Sickingen proposed a method for its extraction from the ore.

The new metal, platinum, thus obtained was in the form of a powder or sponge, which resisted fusion, even in the most powerful furnace, and was thus wholly useless in the arts. Chabaneau undertook the difficult task of obtaining platinum in metallic ingots, in spite of its infusibility. He recognised that this very infusibility would give great value to objects made of this new metal.

Several other chemists of the time had busied themselves with this same problem. The only hope of success appeared to be in alloying platinum with other metals, but this seemed to present insurmountable difficulties, owing in part to the impurity of the platinum ore, and also to the large amount of other metals necessary for its solution. It was early observed (von Sickingen says by Scheffer, who

wrote in 1751) that a small amount of metallic arsenic caused platinum to fuse easily, but the ingot thus obtained was exceedingly brittle. Achard (1779) found that by heating this alloy for a long time at a high temperature the arsenic was gradually volatilised, leaving a mass of platinum in a malleable condition. While his communication to the Berlin Academy is entitled "*Leichte Methode, Gefässe aus Platina zu bereiten*," it was nearly ten years before practical application seems to have been made of the method, and though a letter appears in *Krells Annalen* in 1790 stating that platinum vessels can be bought cheaply of Jeanty in Paris, they were actually very rare and possibly never practically used until after the close of the century. Achard's method seems, however, to have been used industrially by Jeanty as late as 1820, though the method of Chabaneau, rediscovered by Knight and possibly independently by Cock also, came into general use in the first decade of the nineteenth century. The vessels made by Achard's method could never have been satisfactory, especially owing to the difficulty of completely removing the arsenic from the platinum.

Among the nobility who had interested themselves in the founding of the college at Bergara was the Marquess of Aranda. This man (minister of state and general, in 1787 ambassador to Paris) was distinguished among all the nobles for his devotion to science. He held Chabaneau in high esteem, and encouraged him strongly in his projected work upon platinum. He had the government turn over its whole supply of platinum ore to Chabaneau, and furnished him everything in his power for the laborious undertaking. Laborious, indeed, for even to day Dumas says "of all analyses, that of platinum ore is, without contradiction, the most difficult."

In spite of the regal luxury of his laboratory, Chabaneau found at that time in Madrid fewer resources than would to-day be offered by the most unpretentious laboratory in France. Chabaneau was obliged to prepare his own reagents and make his apparatus. Chemistry was still an empiric science, and Lavoisier had only just begun to bring order out of chaos. Further, at this time no one could have suspected that in addition to gold, mercury, lead, copper, iron, &c., the platinum ore contained five more metals, osmium, iridium, palladium, rhodium, and ruthenium, not discovered till 1803 and 1844. Chabaneau found himself contending with six metals where he supposed there was only one, platinum. Inevitable mistakes and innumerable disappointments naturally resulted. He had proved that platinum was malleable, yet occasionally he found it despairingly brittle (this was an alloy with iridium); he knew that it was infusible, incombustible, and unoxidisable, yet he was stupefied to see it at times burn and volatilise (this was the alloy with osmium).

The Marquess of Aranda, appreciating the great interest attaching to the industrial use of a metal of which Spain possessed all the mines, came often to Chabaneau's laboratory, and often found him discouraged and busying himself on other investigations. At such times Aranda, a most genial and lovable character, would console him, encourage him, and in the end bring him back to that which Aranda considered his great task, the investigation of "white gold," as it was then called. Chabaneau would take up with new zeal his tantalising work, and so passed days and nights, months, and years. At last he succeeded in surmounting all difficulties, his wearisome task was rewarded by the discovery of a process by which the metal could be purified. The effectiveness of the method was verified by several repetitions. The enchanted Marquess had him carry it out on a large scale, and came to the laboratory each day with increasing interest. Judge of his astonishment and horror when one day he found Chabaneau in a frenzy engaged in throwing out the door and windows his dishes, flasks, and ores, as well as all the solutions of platinum which he had prepared with so much trouble and difficulty.

The Castilian imperturbability of the Marquess only re-

doubled the French fury of the young chemist. "Away with it all. I'll smash the whole business," he cried in a mixture of French and the patois of Périgord. "You shall never again get me to touch the damned metal." And in fact he broke up all the apparatus of the laboratory.

Really this infantile fury was to some extent justifiable. No one knew then, and indeed few know now, that lime does not precipitate platinum in artificial light, but that in daylight the metal is completely precipitated by this reagent. Chabaneau, working with lime at night, had been enabled to precipitate all the other metals which were present in its solution, while his platinum was left unprecipitated and purified. Repeating the operation by day, platinum and all were thrown down, and he was completely at sea, without being able to suspect the reason.

Three months later, at the home of the Marquess of Aranda there appeared upon a table an ingot some 10 centimetres cube, with a beautiful metallic lustre; it was malleable platinum. The enthusiastic Marquess started to pick it up, but failed to move it. "You are joking," said he to Chabaneau, "you have fastened it down." "No, indeed," said the professor, and he raised the little ingot easily, though it weighed some 23 kilograms. The Marquess had not thought that the light platinum sponge would thus appear as the heaviest of all (then known) metals.

Chabaneau's discovery consisted in compressing the platinum sponge while hot at the moment of its formation, and then hammering it several times while at a white heat. Since platinum is infusible at the highest temperature of a furnace, it is easily recognised how difficult it had been to convert the pulverulent metal into an ingot. This infusibility is, however, only relative, since Deville has since succeeded in fusing the metal with the oxygen-hydrogen blowpipe; but this property, added to a resistance to the action of acids equal to that of gold, evidently entitles platinum to rank with the precious (noble) metals.

It is to be noted that there were two necessary conditions for the preparation of malleable platinum, either of which was useless without the other. First, the metal must be obtained from the ore in a pure condition, for unless separated not only from the base metals, but also from the largest part of the other platinum metals, the sponge can not be welded into a malleable mass; second, while at a high temperature the sponge of pure platinum is easily compressed into a malleable ingot, at low temperatures it has no coherence. Virtually this process, generally attributed to Knight, was in use almost exclusively until the last third of the nineteenth century.

The king, who spent some of his leisure moments dabbling in science, often came to Chabaneau's laboratory and assisted in his experiments. He was very proud to have such a discovery made in his capital, and caused a commemorative medal to be struck in platinum. He also gave Chabaneau a life pension of 2800 piastres (3000 dols.), in addition to his annual stipend of 12,000 livres, but the pension was granted only on the express condition of residence in Spain, and was to be forfeited should Chabaneau leave the kingdom. The letters-patent bear the date of 1783, and thus establish the priority of Chabaneau's discovery officially and in an incontestable manner.

Chabaneau was for some time engaged in preparing large quantities of malleable platinum. Then his patron, Marquess d'Aranda, having been appointed ambassador to France (1787), he was prevailed on to accompany him to Paris, in order to convert under his auspices some of the new metal into ornaments for the crown. Jeanetty, goldsmith to the court of France, and a very able man, had been commissioned for this work, and he sought vainly to discover the process used by Chabaneau. He did, however, discover another method (alloying with arsenic), and employed it with such success that he founded in Paris a manufactory for platinum ware, which prospered down to 1820. At present the method of compression while hot, without alloying, is used, and that of Jeanetty has been abandoned.

It was only two years after this memoir was written that Deville and Debray perfected the method first proposed by Hare in 1838 of fusing platinum in the flame of the oxygen-hydrogen blowpipe. The memoir is somewhat misleading regarding the process of Jeanty (or Jeanetty), for while it is true that he did for many years manufacture platinum crucibles and other vessels by his method, it was early in the century entirely supplanted by the compression method, and it is doubtful if much practical application was ever made of it.

It is then to Chabaneau that belongs all the honour of having first discovered and employed on a large scale the only method which is in use to-day for preparing a metal so valuable for chemistry and the arts, and yet no contemporary writer has recorded the claim of our modest compatriot to the glory of this discovery. I apply to him the term modest, for in spite of all our entreaties he could never be persuaded to put forward his just claims. But to-day, as we have before our eyes the letters-patent of the Spanish government, bearing the date of 1783 and testifying to the discovery made by Chabaneau, we come to lay claim for him to the honour of incontestable priority, and to preserve his memory, ungratefully forgotten by his contemporaries.

About 1790 Chabaneau published a large work on the natural sciences in the Spanish language, which was to have been followed by several others, but which was complete as far as regards his speciality. This work, which demanded so much research, night work, and fatigue of every kind, gravely affected his health, and the court physicians prescribed a return to his native air and a period of complete repose. This rest and our climate affected him so favourably that in a few months his health was wholly regained, and he determined to renounce his pension of 15,000 francs in order to dwell in his fatherland, and to end in this quiet retreat, in the bosom of his family, a life, hitherto passed among strangers in the midst of the most assiduous labours.

Retiring to the country, near Nontron, he sought to live obscurely, but the jury of the central schools of France besought him to accept the chair of physics and experimental chemistry in the Ecole Centrale of Périgueux. The subjects were so seldom taught at this period that Chabaneau felt it the duty of a good citizen to accept the modest position. His course of lectures, which lasted two years, was printed at the expense of the administration, and published in year VII. by Canler at Périgueux.

On the suppression of the central schools he was offered a chair of chemistry at Paris, and his permission was sought to translate and publish his great work; but, well determined this time to live in his quiet retreat, he refused all these propositions, desiring only to live in solitude and to enjoy the repose so needed and so welcome after all his labours.

He died in January, 1842, at the age of 88, and left no descendant bearing his name. He lived tranquilly, isolated from the world, on his country place of Clara, near Nontron, dividing his time, like a sage of antiquity, between rural pursuits and philosophical study.

We knew him only in his declining years, but he was then a fine looking old man, with pleasing and regular features, bearing much resemblance to those of our good and lamented Béranger. His conversation was charming and always instructive. Friend and contemporary of Volney, of Cabanis, of Lavoisier, he was nourished upon their ideas and imbued with their spirit, and they were pleasingly reflected in his conversation.

Thus ends the story which has happily rescued us from oblivion the life and work of one of the gifted early workers in chemistry. That his name had been forgotten is doubtless chiefly due to his own modesty, but in part also to the fact that his labours were largely carried on in Spain, and his only important published work was in that language. Whatever may be the reason, the atmosphere of Spain has never been conducive to the development of science.—*Popular Science Monthly*, January, 1914.

A SIMPLE SUBSTITUTE FOR A LEAD CRUCIBLE
OR CAPSULE.

By F. L. SHARP.

A PIECE of thin lead foil, such as is used for assay purposes, is carefully pressed into the interior of an ordinary porcelain crucible in such a manner that it adapts itself to the shape of the crucible. It is then suitable for testing for silicates. The substance, mixed with calcium fluoride, is put into the crucible, a little concentrated sulphuric acid added, and the whole carefully heated. The issuing vapours are allowed to impinge on a drop of water suspended in the loop of a platinum or lead wire. If a silicate be present a deposit of silica is at once seen in the drop of water. A thin strip of the lead foil may be rolled up and used as a substitute for the platinum or lead wire.

ANOMALOUS ROTATORY DISPERSION.*

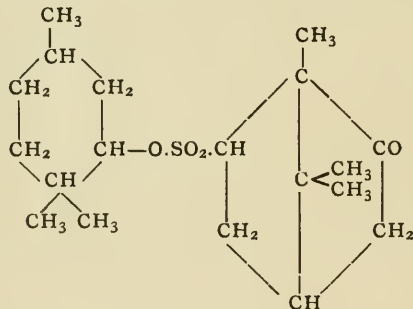
By Prof. LEO TSCHUGAEFF, Royal University, St. Petersburg.

(Concluded from p. 221).

3. We may now turn to the third and last type of anomalous rotatory dispersion.

It was recently shown by the author (L. Tschugaëff, *Berl. Ber.*, 1911, xlv., 2023; L. Tschugaëff and G. Glinin, *Berl. Ber.*, 1912, xlv., 2759) that anomalous dispersion may be produced by the superposition of the partial rotations produced by two asymmetric complexes within the molecule of an active body, the necessary condition being that these partial rotations should be of opposite sign and should possess different dispersion ratios.

As an example of bodies which belong to this type, menthyl β -camphorsulphonate may be cited, the two centres of activity being the menthyl and the camphor radicles:—



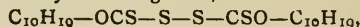
R. W. Wood ("Physical Optics," New York, 1911) has recently pointed out that there must exist a special case of anomalous dispersion which he denotes as "spurious," which is intimately related to the type just alluded to. Wood concluded from theoretical considerations that anomalous dispersion must ensue if we have two electrons in an active molecule, one in the infra-red and the other in the ultra-violet. If these electrons rotate in the same direction, the rotation may be expected to go through a zero value near the middle of the visible spectrum, whilst if they are of opposite sign, one being dextro-rotatory and the other laevo-rotatory, the rotation will have a minimum value. In Prof. Wood's opinion the case of tartaric acid is of this type.

It is well to bear in mind, also, that each anomalous dispersion curve must necessarily be influenced by the superposition of the consequent partial rotations if more than one asymmetric carbon atom (or generally more than

one centre of activity) is present in the molecule of the active substance.

For this reason it is not surprising that there is no complete parallelism between the presence of an absorption band and the appearance of anomalous dispersion in the visible spectrum (L. Tschugaëff and O. Ogorodnikoff, *Zeit. Phys. Chem.*, 1913, lxxxv., 481).

Thus, menthyldixanthogenide,—



and bornyldixanthogenide,—

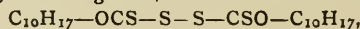


exhibit anomalous rotatory dispersion within the limits of the visible spectrum, whilst the fenchyldixanthogenide (isomeric with the bornyl derivative just mentioned and possessing a similar spectrum) does not possess this property.

In order to clear up the nature of the dispersion curves resulting from optical superposition it is necessary to examine, first, if the superposition rule is generally valid, and, secondly, in what degree these partial rotations themselves are influenced by mere constitutional factors.

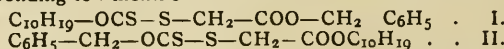
The principle of optical superposition, first suggested by van't Hoff ("Lagerung der Atome in Raume," 1908, III. Aufl., Braunschweig), was subsequently subjected to an experimental test by Guye and Gautier, and by Walden, and recognised as valid (cf. van't Hoff, "Lagerung der Atome in Raume," 1908, III. Aufl., Braunschweig). Recently, however, Rosanoff (*Zeit. Phys. Chem.*, 1906, lvi., 565) and Patterson and his pupils (*Journ. Chem. Soc.*, 1906, lxxxix., 1039; 1907, xci., 705) put forward theoretical objections and experimental evidence against the validity of this principle, their arguments being based on a comparison of the optical rotation produced by the methyl esters of the isomeric diacetyl tartaric acids.

According to the theory of optical superposition the rotation of the ester corresponding with mesotartaric acid should be equal to half of the sum of the rotations produced by the ester of *d* and *l* tartaric acids. The maximum departure from the theoretical value in the experiments of Patterson amounted to 18 per cent. But the rotation values of these esters are largely influenced by the nature of the solvent used, and van't Hoff suggested therefore that analogous experiments should be made in more comparable conditions.

As a matter of fact, experiments performed by Mr. Glebko (*Berl. Ber.*, 1913, xlv., 2752) at my suggestion with *l* menthyl and fenchyl urethanes of the isomeric diethyl tartrates gave much better agreement with theoretical values, the difference varying from 1 to 5 per cent. Consequently, the superposition rule seems to be valid at least to a first approximation.

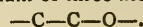
Experiments quite recently performed in my laboratory have shown that the dispersion curve of an active substance is influenced not only by the absorption bands, but by the distance of the centres of activity from the chromophores of the active molecule. Thus, a chromophore group situated in the neighbourhood of a centre of activity may produce anomalous dispersion within the limits of the visible spectrum, whilst if sufficiently remote from such a centre its influence on the shape of the dispersion curve may be small or negligible.

To take an instance, of the two metameric esters corresponding to *l* menthol—



it is only the first (I.) which shows anomalous dispersion in the visible region, the dispersion of the ester II. being quite normal. (This work—not yet published—was performed at my suggestion by Mr. W. Lebedinski.)

Now, in the ester I. the chromophorous group CS—S is separated from the active radicle, $\text{C}_{10}\text{H}_{19}$, only by a single oxygen atom, whilst in the second ester these two radicles are separated by a chain of three atoms,—



* A Contribution to a General Discussion on "Optical Rotatory Power," held before the Faraday Society, March 27, 1914.

The above conclusion is quite analogous with a rule put forward by the author some sixteen years ago (*Berl. Ber.*, 1898, xxxi., 360, 1775, 2451; *Journ. Russ. Phys. Chem. Soc.*, 1897, [II.], xxix., 122, 227; 1898, xxx., 18, 51, 188, 217; 1902, [I.], xxiv., 606) for optical rotations corresponding with one definite ray of the spectrum, namely, the D line of sodium. According to this rule the influence of an inactive substituent introduced into an active molecule at a point sufficiently remote from the centre of activity is very small, but its influence attains its highest value if the place occupied by the substituent is in the neighbourhood of the inactive complex.

NOTE.—These conclusions are by no means altered by the results of the very beautiful work of Messrs. Pickard and Kenyon, which show secondary irregularities in the rotation curves in homologous series at points at which the carbon chain can return upon itself (R. H. Pickard and J. Kenyon, *Journ. Chem. Soc.*, xcix., 45; ci., 620, 1427; ciii., 1923. See also the very remarkable Presidential Address by P. F. Frankland, (*Journ. Chem. Soc.*, ci., 656).

It is particularly noteworthy that the radicles, the introduction of which into the molecule of an active substance causes the rotation values for the most part to be raised (e.g., the radicles with a double linkage, the aromatic groups, &c.), and the chromophores which are responsible for anomalous dispersion possess the same chief feature, for they are both unsaturated groups.

In the author's opinion the modern electronic theory of rotatory polarisation and dispersion created by Drude ("Optik," 1906), is capable of throwing some light on this question, and of giving a rough idea of the influence which the constitutional factors just considered may exert on the sweep of the dispersion curve.

Drude has put forward the idea that optical rotation is due to a peculiar form of electronic motion. He assumes that the dispersion electrons which are capable of being set in vibration by the impacts of the light waves are forced in active bodies to move to and fro in a spiral path instead of along straight lines, the direction of the motion corresponding with the sign of the rotation. This motion is obviously due to the asymmetric distribution of matter within the molecules of the active compounds.

Drude makes no special hypothesis as to the position occupied by the active electrons, but it seems reasonable to suppose that the most active of them are attached to the asymmetric carbon atom itself, or are situated in the immediate neighbourhood of the centre of activity. As regards the other electrons which come into play in rotatory dispersion, we can assume that their activity is diminished with increasing distance from the asymmetric complex.

In the spectrum of colourless saturated organic compounds there seems to exist a very deep band (or several bands) in the inaccessible ultra-violet, and it is very probable that to this band is due the general shape of the "normal" dispersion curve, its "anomalous" portion being restricted to the neighbourhood of the band.

This view is in accordance with the results recently obtained by T. M. Lowry in his very remarkable investigations on both magnetic and optical rotatory dispersion (*Phil. Trans.*, 1912, ccxii., 261; *Journ. Chem. Soc.*, 1913, ciii., 1062; T. M. Lowry and T. W. Dickson, *Journ. Chem. Soc.*, 1913, ciii., 1067; *Proc. Chem. Soc.*, 1913, xxix.). Lowry pointed out that the dispersion of many colourless active compounds in the visible spectrum may be represented by means of an equation given by Drude with but two constants,—

$$a = \frac{k}{\lambda^2 - \lambda_0^2}$$

λ_0 being the wave-length of the remote ultra-violet band.

If, however, the substance in question possesses another absorption band within the limits of the visible spectrum, the dispersion curve becomes anomalous in the accessible spectral region, and even if the selective absorption occurs in the near ultra-violet, as in the case of the ketones above

mentioned, the shape of the curve corresponding to the visible part betrays the neighbourhood of an absorption band, the dispersion ratios assuming abnormally high values.

Let us first turn our attention to colourless compounds, and consider in what manner the different inactive radicles of an asymmetric molecule—



containing but one asymmetric carbon atom, can influence the rotation value and the shape of the dispersion curve.

As we have seen, the chief part of the optical rotation will be produced by the electron (or electrons) attached to the asymmetric carbon atom itself, and will remain in direct relation to the deviation of the spiral path along which the electron moves from a straight line. Now, it may be admitted that this deviation should be proportional to the degree of asymmetry of the molecule as measured by the product of the differences of four constants, K_1, K_2, K_3 , and K_4 , corresponding with the four groups R^I, R^{II}, R^{III} , and R^{IV} of the molecule $CR^I R^{II} R^{III} R^{IV}$, as was originally suggested by Ph. A. Guye ("Etude sur la Dissymétrie Moléculaire," Geneva, 1891) and by Crum Brown (*Proc. Roy. Soc. of Edinburgh*, 1890, p. 181).

$$P = (K_1 - K_2)(K_1 - K_3)(K_1 - K_4)(K_2 - K_3)(K_2 - K_4)(K_3 - K_4).$$

Perhaps we should not be far from the truth if we assume further with Guye that the variables $K_1 \dots K_4$ are functions of the masses of the radicles attached to the asymmetric atom, although we do not know the exact nature of this function; but in any case, if these four groups differ materially in their degree of saturation, we shall still have to consider the influence of another constitutional factor on rotation; thus, it would be expected that strongly unsaturated radicles containing free-movable electrons would exert a considerable influence on the electric field produced by the molecule, the differences $K_1 - K_2 \dots$ being much larger if K_2 corresponds with a saturated group and K_1 to an unsaturated one than if both the groups are nearly equally saturated.

From this point of view it may easily be understood why the influence of unsaturated groups on the rotation values is considerable only when in immediate proximity to the asymmetric carbon atom. (It seems to be permissible in this case, at least to a first approximation, to compare the effects produced on the rotation by different substituents entering into the molecule for one determined wave-length, e.g., for the D sodium line, as has so often been done).

On the other hand, the rotation and dispersion produced by an active molecule—



may be influenced by the vibration of the electrons attached to the radicles, $R^I, R^{II}, R^{III}, R^{IV}$, as well as to the asymmetric carbon atom itself, for the asymmetry of the field within the molecule must cause all these electrons to move along spiral paths. Consequently, each radicle must contribute by means of its electrons to the value of the optical rotation produced by the molecule as a whole, and (the free periods of these electrons being, in general, different) also to the resulting dispersion. It may be noted also that it is by no means necessary that the electrons in the four radicles and in the central atom should rotate in the same direction. Consequently, it seems to be possible that certain bodies containing but one asymmetric carbon atom can exhibit anomalous rotatory dispersion. The anomaly will be due, in this case, to the superposition of the effect produced by the electrons

attached to the different radicles of the same molecule. The question as to whether such cases can be realised in practice can be settled only by experiment, but it is possible that some cases of anomalous rotatory dispersion quite recently noticed by R. H. Pickard and J. Kenyon should be classed in this category (*Proc. Chem. Soc.*, 1913, xxix., 296).

Time will not permit of further discussion of the influence of chemical constitution on the rotatory dispersion in active compounds, but I should like before concluding to touch briefly upon an allied question which claims a very considerable interest.

It was pointed out by Chr. Winther (*Zeit. Phys. Chem.*, 1902, xli., 161; 1903, xlv., 331), and by P. Walden (*Berl. Ber.*, 1905, xxxviii., 345; *Zeit. Phys. Chem.*, 1906, lv., 1), that the dispersion curves of several anomalously dispersing bodies are largely influenced by the temperature at which their rotations are taken and by the nature of the solvent used.

It seems to be the current opinion that this particular behaviour is due to a displacement of equilibrium between the two (or more) different kinds of molecules which are assumed to constitute the active substance.

A quite different hypothesis, however, was put forth recently by R. W. Wood, the distinguished American physicist. He assumes, as previously mentioned, that the anomalous dispersion of tartaric acid may be due to the existence of two active electrons in its molecule.

This hypothesis is in complete accord with the view just put forward, that several electrons may be active in a molecule containing but one asymmetric carbon atom, in which case the rotatory power as well as the dispersion of the substance in question will be equal to the sum of the effects produced by several active electrons.

On the other hand, it is very probable (1) that the configuration of the molecule, and consequently the degree of asymmetry of the corresponding asymmetric field, is a function of the temperature, and (2) that the intensity of this field is not equally influenced in its different parts by the same rise of temperature.

It seems to be quite possible therefore that the influence of different active electrons may become dominant at different temperatures, and that a substance which possesses normal rotatory dispersion at a certain temperature t_1 may become anomalous at another temperature t_2 . It is, however, very difficult in the present state of our knowledge to distinguish between such a case and the case of a mixture of two active bodies which present anomalous dispersion at certain temperatures only.

Similar considerations may apply in relation to the influence of solvents on anomalous rotatory dispersion. It is therefore easy to understand that, from the above point of view, active bodies which are especially sensitive to the influence of the temperature and of the solvents must have a marked tendency to present the phenomenon of anomalous rotatory dispersion.

NOTE.—Quite recently R. H. Pickard and J. Kenyon stated that certain esters containing but one asymmetric carbon atom exhibit anomalous rotatory dispersion at high temperatures as well as in several solvents (*Proc. Chem. Soc.*, 1913, xxix., 296). In the author's opinion this effect may be due to the intramolecular superposition of the effects produced by several active electrons.

Since nearly the whole of the experimental data concerning the influence of temperature and of the solvent on anomalous rotatory dispersion have been derived from derivatives of tartaric and malic acid (*Zeit. Phys. Chem.*, 1913, lxxv., 481, 553), it seemed advisable to undertake analogous experiments with active bodies representing the different types of anomalous dispersion above mentioned. This work has been carried out in my laboratory in conjunction with Messrs. Piquelowsky, Pastanogoff, and Ogorodnikoff. (The details of the experiments of R. H. Pickard and T. Kenyon above mentioned are not yet available).

The results obtained have two important bearings:—Firstly, they show that sensibility to the influence of temperature and to the nature of the solvent is not confined to colourless bodies exhibiting anomalous dispersion of the type of tartaric acid, but occurs also in substances exhibiting Cotton's phenomenon and in those which possess anomalous dispersion due to intramolecular optical superposition.

It may be noted also that this sensibility can be very different in closely related substances. To take an instance, the dispersion of the thioanhydride of the menthyl-xanthogenic acid, $C_{10}H_{19}O-CS-S-CS-O-C_{10}H_{19}$ is very considerably influenced by temperature, while the sensibility of the corresponding fenchyl derivative is quite insignificant, in spite of the fact that both dispersion curves are nearly identical in shape.

Secondly, it follows from our experiments that in many cases the anomalous dispersion curves are shifted by the influence of temperature or by the nature of the solvent in the same direction as in the case of tartaric acid and its esters. For instance, the behaviour of the thioanhydride of menthyl-xanthogenic acid, $C_{10}H_{19}-OCS-S-CSO-C_{10}H_{19}$ towards temperature and the influence of different solvents on the dispersion of menthildixanthogenide, $C_{10}H_{19}OCS-S-S-CSO-C_{10}H_{19}$, may be cited. In both cases the curves are at the same time raised and shifted to the violet end of the spectrum, precisely as Winther and others have observed in the case in the tartaric series. This analogy is a very remarkable one, and whatever its final interpretation may be, there is no doubt that there must exist some intimate relation as to the origin of the anomaly in both cases.

CHEMICAL REACTIONS AT VERY LOW PRESSURES.*

I.—THE CLEAN-UP OF OXYGEN IN A TUNGSTEN LAMP.

By IRVING LANGMUIR.

Continued from p. 225.

1. *Effect of Pressure.*—In every case the value of ϵ was found to be practically independent of the pressure. For example, in the experiment from which the curve in Fig. 2 was obtained, the following values of ϵ were obtained:—

Time, t .	Quantity of O_2 , q .	ϵ .
0	14.09	0.0051
1	10.58	
3	7.59	
5	5.42	
7	3.20	0.0045
9	2.50	
11	1.66	
13	1.05	
17	0.40	0.0049
20	0.25	
23	0.18	

The curve given in Fig. 2 was calculated from Equation 10 by taking $\epsilon = 0.0049$, $A = 0.067$, $v_0 = 1075$. The equation thus becomes:—

$$\epsilon = \frac{0.0554}{t} \log \frac{q_0}{q},$$

where t is the time in minutes. It was from this equation also that the values of ϵ in the above table were calculated. It is seen from Fig. 2 that the calculated curve agrees well with the points determined by experiment.

This independence of ϵ from the pressure has been tested and found to hold for pressures as high as 50 and as low as 0.2 micron.

* Paper read before the New York Section of the American Chemical Society. From the *Journal of the American Chemical Society*, xxv., No. 2.

The fact that ϵ is independent of the pressure means simply that the rate of clean-up is strictly proportional to the pressure; in other words, the reaction acts like a monomolecular reaction.

2. *Effect of Length of Filament.*—Sections A, B, and C were respectively 5, 15, and 47 cm. long, yet as is shown clearly in Tables I., II., and III., the values of ϵ obtained were practically the same from each. This simply means that the rate of clean-up is strictly proportional to the surface of the filament.

TABLE I.—Values of ϵ from Exp. 265.

Temp. of filament.	Section A.	Section B.	Section C.
1270° K	0.0010	0.0011	0.0014
1470	0.0049	0.0049	0.0055
1470	—	—	0.0059
1570	0.0092	0.0091	0.0099
1770	0.021	0.024	0.027
1770	0.025	0.027	0.027
1770	0.026	0.024	—
1770	0.028	—	—

TABLE II.—Effect of Heating Bulb.
Values of ϵ from Exp. 265.

Temp. of filament.	Section B. Temperature of bulb.		Section C. Temperature of bulb.	
	23°.	300°.	23°.	300°.
1270° K	0.0011	0.0012	0.0014	0.0013
1470	0.0049	0.0042	0.0057	0.0053
1570	0.0091	0.0078	—	—
1770	0.0250	0.0183	—	—

TABLE III.—Values of ϵ from Exp. 265.

Temp. of filament.	Section A.	Section B.	Section C.
900—1070° K	0.00036	0.00035	0.00033
1270	—	0.0016	0.0015
1770	0.022	0.026	0.023
2020	0.043	0.049	0.046
2290	0.095	0.068	0.080
2340	—	—	0.084
2520	0.122	0.075	0.090
2770	0.15	0.095	0.115

3. *Effect of Temperature of Filament.*—In Tables I., II., and III. are given the values of ϵ from Exp. 265, in which the apparatus was arranged as indicated in Fig. 1. The separate runs were made in about the order given in the table. The temperatures were obtained from photometer measurements on a lamp made from another piece of the same wire. From the candle power per sq. cm. of surface the temperature was obtained, and from this a curve giving the relation between current and temperature was plotted by use of a formula previously given (*Trans. Am. Electrochem. Soc.*, 1911, xx., 233). After the lamp in Exp. 265 had been exhausted and the filaments aged by heating one-half hour at a very high temperature, the relation between voltage and current, and hence temperature, was obtained. From these data a curve was plotted giving $V \sqrt{A}$ for each of the filaments as a function of the temperature. (Here V = volts; A = amperes). This function remains constant even when the diameter of the filament changes between wide limits, and it was by its use that the temperature measurements were made after the filament had been attacked, to any serious extent, by the oxygen. Towards the end of the experiment the resistances (at 25°) of the three sections of the filament had increased up to the following percentages of the original resistance:—

Section A increased to 142 per cent.
Section B increased to 191 per cent.
Section C increased to 121 per cent.

The areas A were therefore reduced as follows:—

Sec. A reduced to 84 per cent of original surface.
Sec. B reduced to 72 per cent of original surface.
Sec. C reduced to 90 per cent of original surface.

In Table III. corrections were made in ϵ to correspond to these changes in surface. The filaments were reduced very uniformly in diameter, as was apparent from the uniform intensity of the light emitted from them.

The irregularities in the values of ϵ at higher temperatures and in the latter runs are probably due to errors in temperature measurements and to the difficulties in measuring the extremely high rates of clean-up which occurred at the highest temperatures.

TABLE IV.—Rate of Clean-up of Oxygen at Various Temperatures.

Temp. K.	ϵ observed.	ϵ cal. by (12).	ϵ cal. by (26).
1070° K	0.00033	0.00016	0.000171
1270	0.0011	0.00123	0.00124
1470	0.0053	0.00525	0.00528
1570	0.0094	0.0095	0.00953
1770	0.0255	0.0256	0.0256
2020	0.049	0.066	0.0664
2290	0.095	0.148	0.150
2520	0.12	0.26	0.264
2770	0.15	0.42	0.426
3000	—	0.60	0.64
3500	—	1.16	1.28

At 2770° K the rate of clean-up was so rapid with Section C that the quantity of oxygen decreased from 14.90 cu. mm. to 2.64 cu. mm. in three seconds. With Section A, at the same temperature, the gas changed from 7.55 to 2.88 cu. mm. in twelve seconds.

The second column of Table IV. gives the most probable values of ϵ taken from Tables I., II., and III. The data for temperatures from 1220 to 1770 are obtained by taking the means of the values in Table I., these being considered the most reliable, as the filaments had not been altered much by oxidation during these runs. For temperatures above 1770 the highest of the values in Table III. were chosen, for the possible errors would seem to make the observed values too low.

The rate of increase of ϵ with the temperature agreed well with Arrhenius's formula—

$$d \ln \epsilon / dT = A/T^2 \quad \dots \quad (11).$$

The following equation, obtained from the above by integration and choice of suitable constants, was found to be in excellent agreement with the experimental results obtained between 1220 and 1770°,—

$$\log \epsilon = 1.76 - 5940/T \quad \dots \quad (12).$$

The values of ϵ calculated for various temperatures from this equation are given in the third column of Table IV. The deviation of the observed from the calculated results at high temperatures is to be expected, as the above equation leads at 3500° to values of ϵ above unity, and this we know, from the kinetic theory, must be impossible.

(To be continued).

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

THE RUST OF CEREALS.

Prof. Gaston Bonnier has presented two papers before the Academy of Sciences on the question of the propagation of the rust of corn by the germs of the fungus mixed with the grain of the cereals. The first of these papers is by M. Eriksonn, Professor at the University of Stockholm; the second is by M. Beauveric, of the University of Nancy. M. Eriksonn is a partisan of the propagation of the rust by the grain itself containing kinds of cysts of rust. For M. Beauveric, who maintains, on the contrary, that the disease could be propagated by the germs to be found on the surface of the seeds, the question is not solved. It is easy to understand that these researches are of the highest importance for agriculture. But whether it be in one way

or the other that the disease is propagated, it is now an acquired fact that the passage of the fungus of rust of corn by the "epine vinette" or barberry thorn is not indispensable to the propagation of the disease from one year to another.

CULTURES OF *ASPERGILLUS NIGER*.

Prof. Gabriel Bertrand has examined the influence of solutions of salts of silver on the culture of the black mildew or smut of *Aspergillus niger*. This influence is pernicious as far as the dose of one-tenth of a milligram per litre. Below that, although the experiments have been continued to an extraordinary weak dilution of a molecule-gram of argentic salts in 10 milliards of trillions of litres, it is impossible to detect the least acceleration of growth, contrary to what might have been expected according to the theory of toxic excitement, which is thus contradicted.

CAST IRON AND STEEL IN FRANCE.

A very interesting statistic on the production of cast iron and steel by French metallurgy in the year 1913 has just been published by the Comité des Forges. In 1913 France has produced more cast iron and steel than in the preceding years. The production of cast iron in 1913 amounted to 5,122,091 tons compared with 4,871,992 tons in 1912 and 4,426,469 tons in 1911; that is to say, an increase of 250,199 tons above 1912 or 5.1 per cent, and of 695,622 tons more than 1911 or 15.7 per cent. The production of raw steel amounted during the year 1913 to 4,419,241 tons against 4,078,352 tons in 1912 and 3,680,613 tons in 1911; that is to say, an increase of 341,069 tons or 8.3 per cent more than 1912, and 738,628 tons or 20 per cent more than 1911. The increase of the production, both for the cast iron and steel, is then considerable. The production of cast iron has almost doubled in the last ten years; for in 1904 not more than 2,974,000 tons were cast. The factories, having produced in 1913 5,122,091 tons of cast iron, include 156 blast-furnaces, of which at the end of the year there were 126 alight and 30 out of blast. The number of workmen occupied by the factories producing cast iron is about 15,500. As for Germany, the total production of steel in 1913 was 17,613,666 metrical tons. The number of German metallurgic factories is 244. It is thus evident that French metallurgic industry has still much to do to reach the level of the formidable German production.

LIFE WITHOUT MICROBES.

As far back as 1885 Pasteur had begun to wonder if life without microbes was possible. This problem, of the highest interest for bacteriology and biology, has remained unsolved until within the last few years. However, two years ago, in a paper presented before the Academy of Sciences by Dr. Roux, Director of the Pasteur Institute, M. Michel Cohendy showed that he had been able to bring up chickens aseptically. These experiments were much talked about at the time. At the Pasteur Institute other experimenters continued these researches. It is thus that M. Wollman succeeded in raising tadpoles and flies removed from all microbial germs, and that M. Guyenot obtained whole colonies of aseptic flies, which seems really paradoxical, seeing that flies are marvellous agents of propagation of infectious diseases. It is then actually established that animals belonging to the most diverse groups and provided naturally with a rich intestinal flora can be raised in conditions of perfect asepsy without there resulting for them any inferiority when compared with non-aseptic animals placed in observation as witnesses. As far as concerns mammals, two German savants, Nutall and Thierfelder, have shown that young guinea pigs can live perfectly and increase in weight in the absence of microbes. Unfortunately their experiments were very short. They only lasted thirteen days, and so have been open to criticism. That is why Dr. Michel Cohendy wished to extend to guinea pigs his researches on aseptic life. In a communication made to the Academy of Sciences by Dr.

Roux, M. Cohendy indicates the experiments that he has been undertaking for several months past. The guinea pigs are extracted from the uterus by the caesarian operation at a moment as near as possible to the farrowing time. They are immediately placed in an apparatus containing a provision of food, hay, clover, bran, and cakes, all perfectly sterilised. The breeding apparatus is analogous to that used for the chicken. Its structure permits of its being sterilised all at once at a temperature of 120° under pressure of steam. The different openings are shut up with cotton-wool. The air that penetrates into the interior of the cage is filtered through several filters of wadding. The water necessary for the alimentation of the guinea pigs is also sterilised. Lastly, a special apparatus enables the necessary quantity of sterilised milk to be introduced into the breeding cage. When the uterus contains two or several young ones, one or two are kept as standards for comparison. These later are raised in the same conditions of alimentation, and are as the animals that are serving for the experiments but are from their birth exposed to microbial contamination. M. Cohendy weighed the standards themselves. On the other hand, the initial weight of the animal experimented on was given by the difference in the weight of the mother before and after the extraction of the young one. In order to get a good idea of the asepsy of animals brought up in these conditions, the learned doctor, at the end of the experiment, sowed tubes of gelose with fragments of the digestive tube, of the paws, or of other organs of guinea pigs having lived separated from germs. These experiments have been clearly conclusive. M. Cohendy has made a series of nine breedings, four of which lasted sixteen, eighteen, twenty-one, and twenty-nine days. All the guinea pigs were sterile. The aseptic animals developed admirably. Their weight increased on an average from 20 to 33 per cent. On the contrary, the weight of the standards increased only from 8 to 24 per cent in the same periods. It is thus seen that it is possible to raise guinea pigs aseptically. Experiments made lately by Prof. Küster on the aseptic breeding of a young kid agree perfectly with those of Dr. Cohendy. This kid lived twelve days sheltered from all microbes; its weight increased more than that of standards. In a second experiment made by M. Küster, and which lasted thirty-five days, the weight of the young aseptic animal increased 100 per cent. These researches open a new way to the works that require the elimination of the normal microbial flora. In this way the rôle of the diverse species of microbes in the digestive tubes can be studied as well as the diverse microbial affections of intestinal origin, the microbial association, &c. Dr. Michel Cohendy intends to pursue his researches in a new direction.

Royal Institution.—On Tuesday next, May 19, at 3 o'clock, Prof. D'Arcy Thompson will begin a course of two lectures at the Royal Institution on "Natural History in the Classics"; and on Saturday, May 23, Prof. J. W. Gregory will deliver the first of two lectures on "Fiords and their Origin." The Friday Evening Discourse on May 22 will be delivered by Mr. Robert Mond on "The Mortuary Chapels of the Theban Nobles," and on May 29 by Prof. J. C. Bose on "Plant Autographs and their Revelations."

The Celluloid Trade.—The pamphlet "The Celluloid Trade," issued by the Fancy Goods Trade Section of the London Chamber of Commerce, makes out a very strong case against the proposed legislation relating to the storage of celluloid and articles into which celluloid enters. The memorandum calls attention to the exceedingly wide use of celluloid, and the official reports of the London Fire Brigade are quoted showing that in nine years there have been only six fires due to ordinary celluloid goods. Thus it is maintained that there is little, if any, justification for the proposed by-laws, which would be detrimental to the interests of the thousands engaged or concerned in the selling, storage, or manufacture of celluloid.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, April 30, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

"*Presence of Inorganic Iron Compounds in the Chloroplasts of the Green Cells of Plants, considered in Relationship to Natural Photo-synthesis and the Origin of Life.*" By Prof. B. MOORE, F.R.S.

"*Lack of Adaptation in the Tristichaceæ and Podestaceæ.*" By J. C. WILLIS, Sc.D.

"*Genetics of Tetraploid Plants in Primula sinensis.*" By R. P. GREGORY.

"*Action of Certain Drugs on the Isolated Human Uterus.*" By J. A. GUNN.

"*Influence of Osmotic Pressure upon the Regeneration of Gunda ulvæ.*" By D. J. LLOYD.

(a) "*Glossina brevipalpis as a Carrier of Trypanosome Disease in Nyasaland.*" (b) "*Trypanosome Diseases of Domestic Animals in Nyasaland.*" Trypanosoma pecorum. Part III. Development in Glossina morsitans." By Surg.-Gen. Sir D. BRUCE, F.R.S., Major A. E. HAMERTON, Capt. D. P. WATSON, and Lady BRUCE.

"*Studies on Enzyme Action. XXII. Lipase. (IV.) The Correlation of Synthetic and Hydrolytic Activity.*" By H. E. ARMSTRONG, F.R.S., and H. W. GOSNEY.

FARADAY SOCIETY.

March 27, 1914.

GENERAL DISCUSSION ON "OPTICAL ROTATORY POWER."

In addition to the Papers which have already appeared the following communications were read:—

Prof. Dr. HANS RUPE (Basle) read a Paper entitled "*Some Contributions to the Knowledge of the Influence of Certain Groups on Rotatory Power.*"

The optical influence of the saturated alkyl groups is, generally speaking, an insignificant one. There are indeed some exceptions, but they nearly always have a special explanation. We are, on the whole, able to point out their influence as the normal one.

But "the presence of unsaturation leads to an irregularity." The combination of two pairs of double bonds which Thiele calls "conjugated" sometimes has a strong influence on the optical rotation, but when certain radicals, as the CH_3 or the C_6H_5 group, are combined with the central carbon atoms we observe that this strong increasing effect vanishes entirely.

Very curious is the effect of the phenyl group on rotatory power and not easy to analyse. Close to the asymmetric carbon it nearly always increases the optical rotation. But here already we find some exceptions; thus the benzoyl ester of carboxime has a lower rotation than the derivative of phenylacetic or phenylpropionic acid. As the phenyl group is displaced away from the asymmetric carbon atom, its positive effect diminishes until it becomes less than that of an alkyl group; finally the effect may even become negative. The positive influence of the phenyl group is a polar one depending on its electro-negative character, but what is the negative influence?

The most interesting part of the chemistry of conjugation is due to the combination of the double linking with one or two phenyl groups. This combination can produce a very powerful increasing influence on the rotatory power, particularly when it is near the asymmetric carbon, and a great amount of work is done on this subject. Rather similar also is the effect of a combination of the

C:O group with a phenyl nucleus or a carboxyl group pointed out by Hilditch. But the author is not of Hilditch's opinion that the degree of conjugation is here the principal thing and not the distance; he demonstrates by several examples how important is the distance for the influence of a conjugation.

Very particular is the influence of a combination which the author calls accumulation of unsaturated groups, as, for instance, a double linking combined with a phenyl and a carboxyl or two phenyl groups. The rule here is, that such an accumulation has a depressing influence on rotatory power; very seldom only we find the opposite effect.

The author has not been able hitherto to find any satisfactory explanation for both effects of the unsaturated complexes—the increasing and the depressing one. Neither the fact that several unsaturated groups contain more energy than the saturated ones nor the fact that the molecular volume of the unsaturated groups is greater than that of the saturated is a sufficient explanation. The author has also been unsuccessful in his attempts to find an explanation by using the theory of Stark-Kaufmann of the valency-electrons.

The author finally discusses the question of whether optical rotation may be of service in helping to determine the constitution of optically active organic compounds.

Prof. Dr. H. GROSSMAN (Berlin) read a Paper entitled "*Studies in the Rotatory Dispersion of Tartaric Acid and Malic Acid.*"

The phenomenon of so-called anomalous rotatory dispersion, which was first observed in aqueous solutions of tartaric and malic acids, has called forth numerous theories. The early investigations of the influence of organic solvents on the neutral esters of malic and tartaric acids had, however, shown that these apparently exceptional phenomena are frequent, and that they occur always in the neighbourhood of the zero point, i.e., apparently together with optical inactivity, as soon as materials which call forth a tendency to a reversal of the rotation are added to the pure optically-active substance. This tendency to a reversal in the sign of the rotation was traced back to the formation of more or less stable addition-compounds. In the case of the two acids the relations are complicated by the ionisation. Organic solvents which impede the ionisation of the two acids more than water does will therefore resemble in their behaviour more the concentrated aqueous solutions than the diluted solutions or the solutions of the neutral salts. In the two latter instances the rotation increases normally, for tartaric acid and its salts, from the red to the violet end of the spectrum, but an addition of an organic solvent results in general in a diminution of the dextro-rotation, which may become sufficiently strong to produce a lævo-rotatory system. In such cases the sense of the dispersion, which increases to the left of the zero point from the red to the violet in a negative sense, is likewise reversed. The malic acid offers quite analogous relations, in the opposite sense, however. In that case also we observe anomalous rotatory dispersion with a pronounced maximum in the yellow, green, and blue near the zero, at which we must assume the existence of at least two optically-active systems of different rotatory dispersions. The justification of this view is strongly supported by the behaviour of tartaric and malic acids towards concentrated sulphuric acid and phosphoric acid. Of otherwise remarkable results concerning the influence of organic solvents on the rotation of malic acid in particular we accentuate the occurrence of muta-rotation when malic acid is dissolved in benzylalcohol and in mixtures of benzylalcohol, pyridin, and formic acid; the last-mentioned acid displays the same phenomenon when acting as solvent for tartaric acid.

The investigations clearly demonstrate that the observation of the rotatory dispersion always admits of much more reliable conclusions as to the existence of labile addition-compounds in solution than determinations with mono-achromatic light could lead to.

Papers contributed to the discussion by M. G. Bruhat (Paris), Dr. E. Darmon (Paris), and Prof. A. Cotton (Paris) were communicated by Dr. H. Borns.

M. BRUHAT'S Paper was on "*The Rotatory Power of Tartaric Acid.*"

The diverse anomalies which are seen in the variation of the rotatory power of tartaric acid with the wavelength, the nature of the solvent, and the concentration cannot be explained by the existence of an absorption band in the ultra-violet, nor by a purely physical effect of the solvent. They can, however, be accounted for if we assume that there exist in the solutions two active compounds which are in equilibrium with one another, in proportions which vary with the nature of the solvent, the concentration, and the temperature. The author has measured the rotatory dispersion, at different temperatures, of superfused tartaric acid in the absence of any solvent. He shows that the dispersion curves approach the curves for solutions of different concentrations; rise of temperature acts like a dilution, augmenting the rotatory power, displacing the maximum towards the violet, and finally rendering the dispersion normal. The two compounds in equilibrium are therefore tartaric acid itself and a polymer; cryometric observations indicate that the proportion of this latter must be small and its rotatory power high.

Dr. DARMON'S paper was on "*The Existence of Racemic Tartaric Acid in Solution.*"

The rotatory power and the rotatory dispersion of dextro-tartaric acid, in aqueous solution, depend on the concentration. In diluted solutions the rotatory power is strong and the dispersion is normal. In concentrated solutions the rotatory power is feeble and the dispersion is anomalous. The object of the research is to study mixtures, in different proportions, of the dextro-acid and the lævo acid.

The concentration of the solution is chosen so that the concentration of total acid is high and the excess of the one acid (e.g., the dextro-acid) is small. If racemic acid exists in the solution, its rotatory power is nil; the dispersion should be equal to that due to the acid in the excess (i.e., normal). If, on the other hand, racemic acid does not exist in solution, the rotatory power should be that of a mixture of the two acids (dextro and lævo); the dispersion should be that of a concentrated solution (i.e., anomalous).

The experiments justify the second hypothesis. The solution behaves like a mixture of dextro-acid and lævo-acid.

Further, if we mix racemic acid and dextro-tartaric acid, the solution behaves like a mixture of the dextro-acid and the lævo-acid. The solution behaves in every respect as if the racemic acid were dissociated into its two constituents.

Prof. COTTON'S paper dealt with "*The Constitution of Liquid Mixtures and Rotatory Power.*"

A question of particular importance in physical chemistry may be put as follows:—What happens when we mix two pure liquids? One of the theories which have been advanced for the purpose of explaining the properties of these mixtures, such as are not merely additive, may be called a "chemical" theory. This theory assumes that there exist, in the mixture of the two bodies A, A', by the side of molecules of A and of molecules of A', mixed complexes of definite composition. A variant of this theory assumes that there are in the mixture, in addition to the molecules of the two pure substances, also associations AA, which only contain molecules of one kind and whose number varies with the dilution.

In conjunction with H. Mouton the author proposes certain methods of submitting this chemical theory to the experimental test. The first method is based upon the researches of Darmon. The author gives a generalised account of Darmon's considerations, and shows that the magnetic birefractance can, in the application of this method, replace the rotatory power. In either case measurements are made with several monochromatic radiations. The second method consists in measuring successively, in mix-

tures of diverse concentrations, both the rotatory power and the magnetic birefractance; in this case we may limit ourselves to making use of one radiation only. We may investigate, either mixtures containing a body A endowed with both rotatory power and magnetic birefractance, and another body A', inactive and not birefracting; or mixtures containing a body A endowed with rotatory power only, and another substance A' which is only birefracting. This latter case affords more complete information and enables us to distinguish the mixed complexes from the associations.

The simplification which is attained in the problem of the constitution of mixtures by the consideration of the rotatory power (or of the birefractance) is due to the fact that in both these cases we know diluents which are in themselves inactive.

DISCUSSION.

The discussion hinged very largely on the nature and causes of anomalous rotatory dispersion. There is some doubt as to the exact meaning that should be attached to this term, but speaking generally it may be said that rotatory dispersion is regarded as normal when the rotation increases steadily with decreasing wave-length, and as anomalous if in any part of the spectrum it diminishes with the wave-length.

Dr. PATTERSON protested against the artificial character of this distinction, since a curve which was "normal" in one part of the spectrum might easily become "anomalous" in another part of the spectrum. Again, the curves of rotatory dispersion for a substance like methyl tartrate belonged obviously to one family and differed mainly in the position of the maximum rotation. If this fell in the visible part of the spectrum the curves were described as anomalous, but surely they were equally anomalous if the maximum were displaced into the ultra-violet or into the infra-red.

Dr. LOWRY and Mr. DICKSON agreed with this criticism and urged that the only logical distinction was between the simple rotatory dispersion of compounds which obeyed

the law $\alpha = \frac{k_0}{\lambda^2 - \lambda_0^2}$ and the complex rotatory dispersion of compounds which required two or more of these terms. It was impossible to tell by the eye whether a curve was simple or complex, but this point could be tested very easily by plotting $1/\alpha$ against λ^2 , when the points would be found to fall on a straight line if the dispersion were simple, but on a curve if the rotation were complex.

As regards the origin of anomalous rotatory dispersion, Prof. FRANKLAND and Dr. PATTERSON both urged that anomalous rotatory dispersion could be accounted for by the drift of the temperature-rotation curves. If these intersected in a point the dispersion might be normal under all conditions; if, however, they intersected over a range of temperatures the dispersion would be anomalous over this range.

Dr. LOWRY, in reply, maintained that the dispersion curves were fundamental, whilst the secondary curves were secondary. In measuring rotatory dispersion nothing was changed except the nature of the light which was used to test the properties of the substance; when the temperature was changed the chemical character of the liquid might be completely altered owing to the dissociation of complex molecules, and in the case of solutions by the breaking down of compounds of solvent and solute. In cases of simple rotatory dispersion the temperature rotation curves would intersect on the axis of zero rotation; for the whole spectrum to give an equal rotation other than zero would be nothing less than a miracle. In cases of complex rotatory dispersion the temperature curves would naturally intersect over a range of temperatures, but this would be a secondary effect and not the cause of anomalous dispersion.

The view that anomalous dispersion is due to the presence of two or more kinds of optically active molecules was upheld by Prof. ARMSTRONG, who urged the possibility of dynamic isomerism; by Prof. GROSSMAN, who postu-

lated compounds of solvent and solute; by Dr. PICKARD and Mr. KENYON, who had detected anomalous dispersion in naphthyl methyl carbinol, $C_{10}H_7 \cdot CH(OH) \cdot CH_3$, and thought it might contain two isodynamic forms of the aromatic nucleus; by Dr. A. MCKENZIE, who suggested that polymeric forms of tartaric acid might exist (a view also advocated in M. Bruhat's paper on the rotatory power of fused tartaric acid); and by Dr. LOWRY, who stated in the discussion that nitro-camphor, which is known as an example of dynamic isomerism, also exhibits anomalous rotatory dispersion, and that ethyl tartrate, a typical example of a substance having anomalous dispersion, can be fractionated into portions which differ widely in their rotatory power for violet light.

Whilst attention was largely directed to the new developments introduced by the measurements of rotatory dispersion, Prof. FRANKLAND and Dr. MCKENZIE had no difficulties in showing the very valuable results which have been obtained from experiments made with light of only one wave-length. If proof were needed, Prof. Rupe's paper would have been sufficient refutation of any suggestion to the contrary effect.

NOTICES OF BOOKS.

Intermetallic Compounds. By CECIL H. DESCH, D.Sc., Ph.D., F.I.C. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

THE author's wide knowledge of metallography and his marked power of clear explanation have enabled him to produce a valuable monograph on the formation of intermetallic compounds. The literature of the subject contains a large number of unsubstantiated facts, and it requires a sound critical judgment to sift the actual truth from them, as the author has done with great success. The method of thermal analysis is first discussed, and some notes are added upon the microscopical control of the results obtained by its application. The difficulties attending the isolation of metallic compounds are described, and then the physical properties of the compounds are treated, emphasis being laid upon the relations between each individual property and the composition. The attempts which have been made to formulate a theory of the constitution of intermetallic compounds are discussed, and suggestions are made as to lines of research which may prove fruitful. No practical methods of investigation are described, but the monograph gives a very fair and unbiased view of the present state of our knowledge of the theory of this branch of metallography.

Industrial Chemistry for Engineering Students. By HENRY K. BENSON, Ph.D. New York: The Macmillan Company. 1913.

THIS book will be found useful for engineering students who have been through elementary courses in pure chemistry and physics, and wish to study the applications of scientific principles to industrial problems, and to acquire some knowledge of the chemistry of the materials and processes which are of special importance from an engineering point of view. The subjects treated in particular include fuels, clay products, cements, &c., while water, industrial alloys, paints, paving materials are discussed rather less fully. The author appears to have selected his material carefully with a view to its general utility, and although American products and practice are naturally given the chief prominence the book may find useful application in English technical schools. The full bibliographies given at the end of each chapter have been very carefully compiled, and will be of great practical value to chemists and engineers.

A Text-book of Physics. Electricity and Magnetism. Parts I. and II. By J. H. POYNTING, Sc.D., F.R.S., and Sir J. J. THOMSON, O.M., M.A., F.R.S. London: Charles Griffin and Co., Ltd. 1914.

THIS volume contains Parts I. and II. of the fourth book of the authors' text-book of physics, and deals with static electricity and magnetism. It is in every respect fully up to the level of the earlier volumes on the Properties of Matter, Sound, and Heat, and no higher praise can be given to it. The authors have written for those who have no previous knowledge of electricity or magnetism, and teachers of physics and college students will appreciate the exceedingly clear style in which the book is written. This is particularly noticeable in the chapters devoted to the discussion of propositions applying to "inverse square" systems and to stresses in the dielectric. Both in the descriptions of experiments and the working out of mathematical formulæ the authors smooth the path of their readers as much as possible, making the subject intensely interesting and at the same time providing a firm foundation for the study of more detailed and advanced works.

Kapillarchemie und Physiologie. ("Capillary Chemistry and Physiology"). By Dr. H. FREUNDLICH. Second Edition. Dresden and Leipzig: Theodor Steinkopff. 1914. (Mk. 1.50).

THE text of this lecture has been only very slightly altered in the second edition, but recent work has been summarised in an appendix, in which descriptions are to be found of many experimental confirmations of the author's views. The essential features of adsorption phenomena are very shortly discussed, and their importance in physiology is explained, and workers in biochemistry will find that the lecture gives them a readable outline of some aspects of physiological problems. The author has made it clear in the appendix that in some matters of detail his opinions have undergone a certain amount of alteration, and his view of the phenomena is, on the whole, unbiased.

Les Origines Mystiques de la Science "Allemande"). ("The Mystical Origins of 'German' Science") By RENÉ LOTI. Paris: Félix Alcan.

THIS thesis discusses, from a point of view which can hardly be described as free from partisanship, the errors which have been introduced into science by mysticism, and the revival of what may be called a modern variety of mysticism in Germany. For those who are interested in the philosophy of science the monograph will be found to give a detailed account of certain points of view, and the author has evidently searched many sources for his material.

Die Theorie der Strahlung und der Quanten. ("The Theory of Radiation and Quanta"). Transactions of the Solvay Conference, 1911. Translated into German by A. EUCKEN. Halle-a.-S.; Wilhelm Knapp. 1914. (Mk. 15.60).

THE papers read at the Conference held at the suggestion of Prof. Solvay in the autumn of 1911 in Brussels are printed in full in this report together with the discussions that followed them. Unavoidable circumstances have delayed the publication of the report, but in essentials the quanta theory has seen only very slight modifications during the last two years, and its development in matters of detail has been traced down to the end of 1913 in an appendix. The conference was attended by some of the world's leading physicists, and papers were contributed by, among others, Lorentz, Jeans, Planck, Perrin, and Nernst. In the discussions some very interesting points were raised, and physicists will be glad to have so clear and detailed an exposition of the most modern aspects of the quanta theory.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 13, March 30, 1914.

Basic Carbonates of Copper.—V. Auger.—The amorphous basic carbonate of copper, $8\text{CuO} \cdot 5\text{CO}_2 \cdot 7\text{H}_2\text{O}$, the composition of which is very nearly that of a hydrated azurite, is transformed, even in presence of CO_2 under 40 atmospheres, into hydrated malachite with loss of CO_2 , but if these substances are kept under pressures above 3 or 4 atmospheres the transformation into azurite takes a period of time which varies, according to the pressure, from some days to some months. On the other hand, the transformation into azurite is very rapid if a small quantity of azurite is added to start the reaction. Azurite can be obtained rapidly and in large quantity if small portions of a soluble salt of copper are added to a solution of $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$ containing azurite in suspension. The double salt, $\text{CuNa}_2(\text{CO}_3)_2 \cdot 23\text{H}_2\text{O}$, when subjected in presence of a little water to the action of CO_2 under a pressure of 40 atmospheres, gives, after a few days, a mixture of azurite and NaHCO_3 . The anhydrous salt, $\text{CuNa}_2(\text{CO}_3)_2$, can be obtained by heating on the water-bath a very concentrated solution of $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$, saturated with the hydrated salt.

Heats of Formation and other Properties of Alkaline Protosulphides.—E. Rengade and N. Costeau.—The absolute densities of the alkaline sulphides at the temperature of the laboratory are:— Na_2S , 1.856; K_2S , 1.805; Rb_2S , 2.912. The heats of solution are:—

$\text{Na}_2\text{S sol.} + \text{H}_2\text{O} = \text{Na}_2\text{S diss.}$		+15.5 cal.
$\text{K}_2\text{S sol.} + \text{H}_2\text{O} = \text{K}_2\text{S diss.}$		+22.7 cal.
$\text{Rb}_2\text{S sol.} + \text{H}_2\text{O} = \text{Rb}_2\text{S diss.}$		+24.6 cal.

These numbers increase regularly with the atomic weight. The heats of formation are:—

$\text{Na}_2\text{ sol.} + \text{S sol.} = \text{Na}_2\text{S sol.}$		+89.7 cal.
$\text{K}_2\text{ sol.} + \text{S sol.} = \text{K}_2\text{S sol.}$		+87.1 cal.
$\text{Rb}_2\text{ sol.} + \text{S sol.} = \text{Rb}_2\text{S sol.}$		+87.1 cal.

The heats of formation decrease with the atomic weight. The equality of the two last results is fortuitous. The three sulphides are not isomorphous.

Precipitation of Alumina in presence of Fluorides.—H. Cavaignac.—When alumina is determined in presence of hydrofluoric acid the acid is incompletely eliminated even after repeated heating with sulphuric acid; the precipitation with ammonia is thus incomplete, more so when the solution is heated than in the cold.

Salicylic Nitriles.—MM. Cousin and Volmar.—Three different substances have been described under the name of salicylic nitrile or *o*-cyanphenol:—(i.) The true nitrile, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{OH} \text{ (I)} \\ \text{CN} \text{ (2)} \end{smallmatrix}$, fusing at 98° . (ii.) A substance fusing at 195° , prepared by Grimaux by dehydrating salicylamide with phosphoric anhydride. (iii.) A substance fusing at 300° , isolated by Limpricht, and regarded by Grimaux as a polynitrile. The authors have proved that the substance fusing at about 200° is identical with disalicylamide, while Grimaux's polynitrile is really a trioxyltriphenyltriazine, which can be converted into a trioxyltriphenylglyoxaline of empirical formula $\text{C}_{21}\text{H}_{16}\text{O}_3\text{N}_2$.

Atti della Reale Accademia dei Lincei.
Vol. xxiii. [i.], No. 4, 1914.

Behaviour of Boric Ethers with Alcoholates.—Livio Cambi.—By acting with boric ethers on solutions of alcoholates the author has prepared the boron-oxyethyl

salts of sodium, lithium, potassium, and calcium; the boron-oxyethyl salts of sodium, potassium, thallium (thallous), and the boron-oxypropyl salt of sodium. The study of the properties of these substances shows that they frequently contain alcohol of crystallisation, and in the majority of cases there is not a whole number of molecules of alcohol of crystallisation to one molecule of salt. The compounds are stable, and behave like true salts.

MISCELLANEOUS.

Royal Society.—At the meeting on May 7, 1914, the following candidates were elected Fellows of the Royal Society:—E. J. Allen, R. Assheton, G. T. Bennett, R. H. Biffen, A. E. Boycott, C. Cuthbertson, D. H. Dale, A. S. Eddington, E. J. Garwood, H. H. Havelock, T. M. Lowry, D. N. Patan, S. Ruhemann, S. W. J. Smith, T. E. Stanton.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 4th inst.; Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Sir John H. Biles, Mr. R. C. Bussell, Mr. J. Carmichael, Mr. R. L. Cookson, Mr. M. S. Napier, and Miss K. O'Sullivan were elected Members. The Chairman announced that a legacy of £100 had been received from the Executors of the late Mrs. Singleton. The special thanks of the Members were returned to Mr. R. Pearce for his donation of £100 to the Fund for the Promotion of Experimental Research.

MEETINGS FOR THE WEEK.

TUESDAY, 19th.—Royal Institution, 3. "Natural History in the Classics," by Prof. D'Arcy W. Thompson C.B.

— Royal Society of Arts, 4.30. (Cobb Lecture). "The Singing of Songs, Old and New," by H. Plunket Greene.

WEDNESDAY, 20th.—Royal Society of Arts, 8.30. "The Channel Tunnel and its Early History," by J. C. Hawkshaw.

— Microscopical, 8. Exhibition of Microscopic Aquatic Life.

THURSDAY, 21st.—Royal Institution, 3. "Identity of Laws, in General and Biological Chemistry," by Prof. Svante Arrhenius, D.Sc., &c.

— Royal Society of Arts, 4.30. "The Indian Census of 1911—Ethnography and Occupations," by E. A. Gait.

— Royal Society. "Effect of the Magnetron in the Scattering of α -Rays," by W. M. Hicks. "Luminous Vapours Distilled from the Arc, with Application to the Study of Spectrum Series and their Origin," by Hon. R. J. Strutt. "Ionisation of Gases by Collision and the Ionising Potential for Positive Ions and Negative Corpuscles," by W. T. Pawlow. "Determination of Elastic Limits under Alternating Stress Conditions," by C. E. Stromeyer. "Emission of Electricity from various Substances at High Temperatures," by G. W. C. Kaye and W. F. Higgins.

— Chemical, 8.30. "Ionisation and the Law of Mass Action—Part III., Utilisation of the Osmotic Data and a New Dilution Law," by W. R. Bousfield. "Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus," by J. Kenner. "Some Indazole Derivatives," by R. Curtis and J. Kenner. "Viscosity of Sugar Solutions," by H. Green. "Compounds of Phenanthraquinone with Metallic Salts," by J. Knox and H. R. Innes. "Quinone-ammonium Derivatives—Part III., Dihaloid, Monoazo-, Bisazo-, Nitrotriazol-, and Bistriazo-compounds—Attempts to prepare Derivatives containing an Asymmetric Quinivalent Nitrogen Atom," by E. Meldola and W. F. Holley.

FRIDAY, 22nd.—Royal Institution, 9. "The Mortuary Chapels of the Theban Nobles," by Robert Mond, M.A., &c.

— Physical, 5. "Volatility of Thorium Active Deposit," by T. Barratt and A. B. Wood. "Passage of α -Particles through Photographic Films," by H. P. Walmsley and W. Makower. "Null Method of Testing Vibration Galvanometers," by S. Butterworth. "Experiments with an Incandescent Lamp," by C. W. S. Crawley and S. W. J. Smith.

SATURDAY, 22nd.—Royal Institution, 3. "Fiords and their Origin," by Prof. J. W. Gregory, F.R.S., &c.

THE CHEMICAL NEWS.

VOL. CIX., No. 2843.

RADIO-ATOMS: THEIR ATOMIC WEIGHTS AND VALENCIES.

By F. H. LORING.

It seems probable that the radio-elements are made up of associate atoms differing in atomic weight, and that they are exactly whole numbers taken from a Rydberg atomic-weight series (see CHEM. NEWS, cix., 169).

The branching in the thorium series at thorium C suggests the possibility that, at this point, the associates virtually part company, and that the respective end-products may be considered as consisting of homogeneous whole-number atomic-weight atoms, standing in proportionate numbers to each other in the same ratio as the products

thorium D and thorium C₂, namely, 0.35 : 0.65 per cent, i.e., as 5 to 9. Then thorium itself should be a mixture: Th²³⁵₅ + Th²³¹₉. The mean value is 232.428, which is in agreement with the present accepted value for thorium, namely 232.42.

Assuming, therefore, for example, that thorium emanation has associates of atomic weights 223 and 219 in the above proportion, then it seems probable that the radium and actinium emanations are also made up from exactly the same Rydberg numbers, but in a different proportion.

Hönigschmid (*Acad. der Wiss. Wien.*, Jan. 22, 1914), in a recent determination of the atomic weight of uranium, gets the value 238.175, which seems too low, as the present accepted value is 238.5 (Richards). A mean between these two values would be 238.33, which is close to a mean of six variable measurements by G. de Coninck (*Comptes Rendus*, 1912, clv., 1511), namely, 238.4.

Taking, therefore, the value 238.33 as a probable one the ratio of the associates would be 1 : 5. Moreover, if the values be of the right order, then the products should probably lie in approximate alignment when tabulated, so that, for example, RaEm, ThEm, and AcEm are in the same horizontal zone, apart from their valence-position.

The accompanying table shows the atomic weights,

VALENCIES.						RYDBERG Nos	VALENCIES.						
0	I	II	III	IV	V		0	I	II	III	IV	V	VI
						5 239 5							
						9 235 1							
232.42					Th								238.33
						231							234.33
228.42					Th ₁ →Th ₂ →RdTh								230.33
						227							226.33
224.42					ThX								222.33
						223							218.33
220.42					ThEm								214.33
						219							210.33
216.42					ThA								206.33
						215							
212.42					ThC ₂ →ThC→ThB								
						211							
208.42					END→ThD								
					END	207							

VALENCIES.						RYDBERG Nos	VALENCIES.						
0	I	II	III	IV	V		0	I	II	III	IV	V	VI
						5 239 5							
						9 235 1							
						231							
						227							
						223							
						219							
						215							
						211							
						207							

VALENCIES.						RYDBERG Nos	VALENCIES.						
0	I	II	III	IV	V		0	I	II	III	IV	V	VI
						5 239 5							
						9 235 1							
						231							
						227							
						223							
						219							
						215							
						211							
						207							

VALENCIES.						RYDBERG Nos	VALENCIES.						
0	I	II	III	IV	V		0	I	II	III	IV	V	VI
						5 239 5							
						9 235 1							
						231							
						227							
						223							
						219							
						215							
						211							
						207							

VALENCIES.						RYDBERG Nos	VALENCIES.						
0	I	II	III	IV	V		0	I	II	III	IV	V	VI
						5 239 5							
						9 235 1							
						231							
						227							
						223							
						219							
						215							
						211							
						207							

VALENCIES.						RYDBERG Nos	VALENCIES.						
0	I	II	III	IV	V		0	I	II	III	IV	V	VI
						5 239 5							
						9 235 1							
						231							
						227							
						223							
						219							
						215							
						211							
						207							

VALENCIES.						RYDBERG Nos	VALENCIES.						
0	I	II	III	IV	V		0	I	II	III	IV	V	VI
						5 239 5							
						9 235 1							
						231							
						227							
						223							
						219							
						215							
						211							
						207							

VALENCIES.						RYDBERG Nos	VALENCIES.						
0	I	II	III	IV	V		0	I	II	III	IV	V	VI
						5 239 5							
						9 235 1							
						231							
						227							
						223							
						219							
						215							
						211							
						207							

VALENCIES.						RYDBERG Nos	VALENCIES.						
0	I	II	III	IV	V		0	I	II	III	IV	V	VI
						5 239 5							
						9 235 1							
						231							
						227							
						223							
						219							
						215							
						211							
						207							

VALENCIES.						RYDBERG Nos	VALENCIES.						
0	I	II	III	IV	V		0	I	II	III	IV	V	VI
						5 239 5							
						9 235 1							
						231							
						227							
						223							
						219							
						215							
						211							
						207							

VALENCIES.						RYDBERG Nos	VALENCIES.						
0	I	II	III	IV	V		0	I	II	III	IV	V	VI
						5 239 5							
						9 235 1							
						231							
						227							
						223							
						219							
						215							
						211							
						207							

VALENCIES.						RYDBERG Nos	VALENCIES.						
0	I	II	III	IV	V		0	I	II	III	IV	V	VI
						5 239 5							
						9 235 1							
						231							
						227							
						223							
						219							
						215							
						211							
						207							

VALENCIES.						RYDBERG Nos	VALENCIES.						
0	I	II	III	IV	V		0	I	II	III	IV	V	VI
						5 239 5							
						9 235 1							
						231							
						227							
						223							
						219							
						215							
						211							

valencies, &c., as the result of this study. Mesothorium 1 and mesothorium 2 are abbreviated respectively: Th₁, Th₂.

It will be seen that the valence-positions of the radio-elements are in accordance with the experimental determinations of valency, being, in fact, a modified form of the Russell-Fajans-Soddy classification, based on the experimental work of G. von Hevesey, Fleck, and others.* It is to be noted that uranium Y is placed in the same atomic-weight and valence-position as uranium X₁. These elements are supposed to be isotopic (see Soddy, *Phil. Mag.*, 1914, xxvii., 215). Uranium Y arises either from uranium 1, taking its place with uranium X₁, or from uranium 2, taking its place with ionium; but uranium Y has not yet been found to give α -rays, so its position with reference to actinium is uncertain. Actinium 1 is, of course, hypothetical. Ac₂ = actinium.

The probable fact that the thorium series is made up of associate atoms differing in atomic weight, which do not become apparent until a species of dissociation sets in towards the end of the transformation process, implies, by analogy, that the equivalent in the right-hand group would be the re-union of the radium and actinium families from, say, uranium Y downwards. If such be the case, then actinium emanation would consist wholly of atoms of atomic weight 223, whilst radium emanation would be equally homogeneous, consisting of atoms of atomic weight 219 each.

This can hardly be the case, as the very small number of atoms (relative to the whole) from one branch product, radium C₁ (-0.0003 per cent), is one-fifth of the number from the other, actinium C (=0.0015 per cent), suggesting that these are homogeneous separations like that assumed at thorium C, but not carried out to anything like completion as in the thorium series.

Moreover, Hönigsmid's value for the atomic weight of radium, 225.97, is against the idea which would assign a value of 223 or 227 to this element. It is worth remarking in this connection that 226 is not a Rydberg number. The Curie-Ramsay value, 226.4, is also favourable to the former view.

Prof. Soddy has pointed out that the 6 end-products are probably isotopic, and may represent the composite element, lead, which has a mean atomic weight of 207.10.

Taking into account the relative percentages of the products, both in the three main series and at the C-branches, the summation in mean of all the end-products yields the atomic weight value 207.

Commenting on the genesis of the elements, the well-known pendulum conception, due to Crookes, is reasonable when rightly interpreted, since the energy stored in the atom has doubtless an origin in some great cosmic process, and there is no reason why a few atoms, overcharged as it were, cannot give up their energy and thus reveal the original process, or rather continue the process far enough to simulate the recoil of the final swing of the pendulum, although the state represented by the oscillating pendulum has long since ceased to exist.

I think, therefore, that the complexity of lead might be considered, in a sense, accidental, since the process of element-formation at the end of the Periodic series has over-reached itself, and, by a reflex action, as if by an irregular backward final slump or recession of the pendulum, has laid down a group of elements that happen to synchronise, or "slump together" at lead; consequently, it would not be a correct extension of the process to carry the complexity of lead down through the entire

Periodic Table. Probably, however, many of the elements have a complexity like that of thorium. In fact, if the above analysis be correct, the inference is undoubtedly that the common elements have *two* types of atoms in many cases, but not necessarily *more* as in the case of lead.

April 15, 1914.

DRY AND WET STRENGTHS OF PAPER AND PAPER YARNS.

By CLAYTON BEADLE and HENRY P. STEVENS.

As far as we know, attempts to determine wet strength of paper have been confined almost entirely, if not wholly, to paper merely in a damp condition; that is, with a limited amount of moisture such as would be imparted to paper by placing it between damp cloths or in atmospheres more or less saturated with moisture, and tests have been made showing the variation in strength of paper in comparison with the amount of moisture which it retains under such circumstances.

Also numerous tests have been made showing the relationship of strength and degree of atmospheric saturation with that of the hygroscopic moisture in the papers of different compositions. These latter determinations have led to the unanimous conclusion by all observers that there is a certain percentage of hygroscopic moisture for all papers (which is a somewhat variable figure according to the nature of the material) at which a maximum strength is obtained. This condition is perhaps arrived in an ordinary medium room temperature between 70 and 80 per cent atmospheric saturation.

Ninety-nine per cent of the paper produced for ordinary commercial purposes has no strength whatever after immersion in water; that is, with such papers there is not sufficient strength to indicate anything on a testing machine. Therefore the strength of a paper after immersion in water, for obvious reasons, has not been investigated. There is no strength in most papers after prolonged immersion in water, even when rosin sized or gelatin sized; but a paper can be made to possess strength even on water immersion if gelatin sized and subsequently treated with formalin to render the gelatin insoluble. Vegetable parchment, which is produced by passing a water-leaf paper through sulphuric acid and subsequent washing and drying, is also a form of paper which possesses some considerable wet strength. There are other papers, such as photographic paper, which require to have some strength on immersion in water; such papers are prepared by special processes. But in the ordinary course of manufacture it is only in the domain of very strong paper that we can look for any appreciable strength on immersion. In passing, we should not forget the importance of high wet strength for many kinds of bag and wrapping paper used for goods which are either moist or require protection from moisture.

There is one kind of paper now coming into extensive use where wet strength would be a most welcome quality, namely, that used in the manufacture of paper yarns.

Table I. shows tests on papers as at present used for paper yarns.

TABLE I.—Test on Papers as at present Used for Paper Yarns

Papers.	Tested.	Substance in grms., per square metre.	Breaking strain, in grms., per inch wide.	Breaking length, in kilometres.
Brown Kraft	Dry	49	9035	8.42
	Dry	41	9950	9.70
	Wet	41	0	0
Yellow Kraft	Dry	44	9850	9.60
	Wet	44	635	0.58

The figures given in this and subsequent tables are the average of ten independent tests. These are the very

* In the Jan., 1914, issue of *Le Radium*, the valencies of practically all the radio-elements except UrY, UrX₂, RaC₂, RaC', AcC₂, AcD, ThD, and ThC₂ are tabulated. The valencies above given are in agreement with these valencies, except in the case of the B-members and RaD, which are indicated as divalent instead of tetravalent, as here shown. The idea of assigning what might be termed complementary valencies to the lower half of the table suggests itself, in which case the values 0-1-2-1-2-3-2, or [8]-7-6-5-5-3-2, may be considered in the light of experiment. By assigning the latter numbers to the lower half of the table, the entire classification agrees with Soddy's group-numbers for the radio-elements.

TABLE II.—Tests on Paper Yarns now on the Market.

Paper.	Tested.	Width of strip. Mm.	Weight, in grms., per metre length.	Number of twists per metre.	Breaking strain, in grms.	Breaking length, in kilometres.	Relative strength when highest = 100.	Diminution in strength as the result of wetting Per cent.
Swedish Kraft ..	Dry	7	0.200	350	1278	6.40	77	
	Wet	7	0.200	350	940	4.70	56	27
Swedish Kraft ..	Dry	7	0.470	450	2189	4.66	56	
	Wet	7	0.470	450	1976	4.20	50	10
Swedish Kraft ..	Dry	6	0.250	400	2081	8.33	100	
	Wet	6	0.250	400	1135	4.55	55	45
Swedish Kraft ..	Dry	4	0.195	200	1590	8.16	98	
	Wet	4	0.195	200	635	3.26	40	59

strongest papers obtainable. In the dry state they possess a breaking length in the neighbourhood of 10 kilometres, but it will be observed that one of the papers has a breaking length of 0 and the other a breaking length which is only about 6 per cent of that of the dry paper.

When paper is twisted, as in the case of paper yarn, the properties as regards wet strength after immersion are altered. If a piece of paper yarn cloth is immersed in water, say, for twenty-four hours and examined, it will be found that it has very considerable strength. In fact, from a hand examination it appears as strong after immersion. As regards its behaviour under water, it would almost appear that the yarn was made from natural fibres. If now a piece of the yarn is stripped from a closely woven paper yarn fabric and pulled, it would be observed that it has some considerable wet strength, but not so much as might be inferred from the general handling of the wet fabric. Untwist the yarn when it will be noticed that the strip of paper comes apart without any exertion whatever; in other words, the wet strength of a paper yarn cloth is not due to the wet strength of the paper from which it was produced but from the fact that the fibres of the paper are twisted, and the twisted yarn is then woven. The paper yarn cloth on immersion has no cohesion among the fibres in the sense that that paper has that has lost its felting qualities as it is understood by paper makers, and although the average length of the fibres may be 1.0 mm. the paper yarn cloth depends almost entirely for its wet strength upon the peculiar juxtaposition of these short fibres as the result of (a) the way they have been disposed when in course of felting together upon the wire of the paper machine; (b) the twisting of the strip; (c) the weaving. These combined agents result in the formation of a textile product the length of the ultimate fibre of which must be exceedingly small in comparison with that of most textile products. Directly the fibres of the paper are placed more or less parallel by the untwisting of the yarn then the wet strength becomes practically nil.

Table II. gives particulars of paper yarns tested, both dry and wet. They are all produced from Swedish krafts. The width of the strip and the weight of the yarn per metre is given, as well as the twists per metre. Also the actual breaking strain of the yarn in grms., which is calculated to breaking length in kilometres, and, for purposes of comparison, the relative breaking lengths are given with the highest at 100, and in a final column the diminution in a strength as the result of wetting.

It will be observed that the wet strength is at least half the dry strength—in fact, on an average about two-thirds the dry strength, whereas the paper from which these yarns are produced (Table I.) the highest wet strength is only 6 per cent, or less than one-fifteenth part of the dry strength.

The chief object of this investigation was to determine the qualities of Hedychium paper for its suitability for paper yarn. Table III. gives figures for paper yarns made from Hedychium paper. The Hedychium paper was produced on a paper machine under our direction. The paper had a substance of 42.5 grms. per square metre and possessed parchment-like and self-sizing qualities. The breaking length of the paper in the direction of the web

was 10.03 kilometres—rather greater than that of the strongest Swedish kraft, but, unlike the Swedish kraft, it possesses considerable wet strength after prolonged immersion. The wet strength of this paper was 1.58 kilometres.

TABLE III.

Tested.	Width of strip.	Weight of yarn, in grms., per metre.	Breaking strain, in grms.	Breaking length of yarn, in kilometres.
Hedychium yarn made by Beadle and Stevens in London ..	Dry	6	0.289	2210
	Wet	6	0.289	1415
Hedychium yarn made on German machine..	Dry		0.264	1883

It will be observed, on comparing the above figures for the Hedychium paper with those of Hedychium paper yarn produced therefrom, that the yarn has diminished in dry strength by about 34 per cent, if the first of the yarns is taken, but has very much increased in wet strength as the result of the twisting. Thus the wet strength of the Hedychium paper at 15 per cent of its dry strength and the Hedychium yarn produced therefrom is 64 per cent. We have already shown that many fibro-vascular bundles and natural fibres, on prolonged immersion in water, lose quite as much as this when tested for wet strength, but of course such fibres are tested in an untwisted condition.

TABLE IV.—Hedychium Yarns produced by Spinning from Undried Paper directly after Couching.

Time of beating. Hours.	Tested.	Weight of yarn, in grms. per metre.	Breaking length, in metres.	Relative breaking length when highest = 100.	Loss of strength due to wetting. Per cent
3	Dry	0.415	3.66	76	
3	Wet	0.415	2.05	43	44
3½	Dry	0.370	4.73	99	
3½	Wet	0.370	2.12	44	55
4	Dry	0.400	4.80	100	
4	Wet	0.400	1.79	38	62

Comparing the above Hedychium yarn figures with yarns produced from Swedish kraft, it will be noticed in the latter that the average diminution in strength from dry to wet is about the same, namely, 36 per cent. The actual dry breaking length of Hedychium yarn (average, Table III.) is 7.37 kilometres, and the average of the Swedish kraft yarn is 6.80 kilometres (Table II.). Thus, already, although we have only reached the initial stages of Hedychium yarns, a better result has been obtained from Hedychium than has been obtained from the best Swedish kraft. As the Hedychium paper from which the yarns were produced had a breaking length of 10.03 kilometres the Hedychium yarn has about 73 per cent the strength of the paper, and a somewhat similar diminution in breaking length as the result of converting strips of paper into yarn is to be noted in the case of Swedish kraft now on the market. Early published figures show quite different results to this; in fact, they show *increase* in strength as the result of conversion of paper into yarn. In spite,

however, of the diminution of strength as the result of the process according to modern practice the yarns and fabrics are much stronger now than they were some years ago.

Further tests were made on Hedychium paper stock which had been treated in a somewhat different manner, the object being to ascertain what kind of result would be obtained by twisting wet couched stuff without previous drying. The wet stuff and that made before couching was cut into ribbons by means of a water jet just before couching. After couching it contained about 43 per cent water, twisted and dried, and the breaking strain, both wet and dry, performed on each lot. The results of this are given in Table IV. In order to find out what effect the time of beating would have the yarn was made up from beaten three, three and a-half, and four hours. At three hours some of the stuff was made into paper by drying in the ordinary way, and tested for the qualities of the paper produced. The paper gave a dry breaking length of 6.8 kilometres, and had a substance of 45 grms. per square metre. It is quite evident that this stuff was not beaten in the best way to suit the paper yarn production. A point of interest here is that by cutting with water jet, couching, and twisting wet (*i.e.*, without previous drying over the drying cylinders), produces a yarn after three hours beating which is very much weaker than yarns produced from paper made in the ordinary way and then slit and twisted, but as the beating is prolonged from three to four hours the breaking length increases, and might have still further increased with further beating. The wet breaking length of the yarn so produced remained almost constant with but slight reduction up to four hours, but, relative to the dry strength, the wet strength is much diminished as the beating is prolonged. Thus, at three hours the reduction in strength as the result of wetting is 44 per cent, at three and a-half hours 55 per cent, at four hours 62 per cent.

As the paper passed over drying cylinders had a dry strength of 6.8 kilometres, but when converted into yarn (at three hours) 3.66, the actual diminution in dry strength from paper to yarn is greater when the water jet is used and no drying cylinders than when finished paper is converted into yarn as it is by modern practice. This is extremely fortunate because modern practice is a great simplification over many of the early attempts. No doubt a great deal as regards qualities of finished yarns depends upon what would appear to be small details, such as the amount of tension on the thread at the moment of re-moistening, twisting, and subsequent drying. Such details are of vital importance in the production of cellulose monofilaments, &c.

There is also the question of substance of paper (*i.e.*, number of grms. per square metre) coupled with width of strip which require further and systematic study. Of course the count of a yarn can be increased by increasing either the substance of the paper or its width, or both. We have already found that the best strength is got from a beaten pulp at some given substance; the general idea now is to employ a paper of from 40 to 44 grms. per square metre, and to vary its width in order to obtain the necessary weight in the yarn. Of course we also have to take into consideration the amount of twist as affecting the weight of the yarn. The great factor, however, in our opinion which has accounted for so much improvement in the quality of the yarn is the improvement in the strength and other physical qualities of the paper which is now procurable for the purpose. The early paper was more bulky and open; consequently it possessed poor strength, but was somewhat improved as the result of its conversion into yarn. The present paper is of the quality known as kraft, a thin strong rattle paper which loses some of this strength by conversion into yarn. But the initial strength of the paper is now so great and the handling qualities of same so excellent as to not only result in the production of much better yarns (in spite of some diminution in strength as the result of the process), but by reason of the use of this class of paper the output of the machines can be much increased by faster running, and the whole process of paper yarn production greatly simplified.

CHEMICAL REACTIONS AT VERY LOW PRESSURES.*

I.—THE CLEAN-UP OF OXYGEN IN A TUNGSTEN LAMP.

By IRVING LANGMUIR.

Continued from p. 235.

4. *Effect of Temperature of the Bulb.*—The conditions which prevail during the reaction of the oxygen with the tungsten in the present experiments differ in several essential features from those which obtain in ordinary reactions between solids and gases at atmospheric pressure.

The pressures we deal with are so low that the normal free path of the molecules is between about 1 and 10 cm. This means that relatively few of the oxygen molecules which travel from the surface of the bulb to the filament strike other molecules on the way. With the relatively small surface of the filament as compared with that of the bulb, the chance that a molecule leaving the filament should get back to the filament without first striking the bulb several times is negligibly small. The average velocity of the oxygen molecules striking the filament is therefore not perceptibly influenced by the temperature to which the filament may be heated. In other words, the filament may be at one temperature and the oxygen with which it comes into actual contact may be at a totally different temperature. At ordinary pressures this would be quite impossible, for the gas, within a layer many hundreds of times thicker than the length of the free path, would be heated nearly to the temperature of the filament, so that the gas in actual contact with the metal would be practically at the same temperature as the metal itself. That there is no great temperature drop at the surface between a metal and a gas at ordinary pressures has been amply proven (see Knudsen, *Ann. Phys.*, 1911, xxxiv., 593).

A direct experimental indication that the behaviour of a gas at low pressures may be quite different from that at high pressures is easily obtained. For example, we find that with nitrogen at atmospheric pressures or even down as low as 100 microns, there is a sudden and marked increase in pressure upon lighting the filament. When, however, the pressure is 10 microns or less, there is no indication whatever on the McLeod gauge of any such change in pressure upon lighting the filament, although the sensitiveness of the gauge would be ample to detect such a change if it were relatively nearly as great as at higher pressures.

All of our previous knowledge of reactions between solids and gases is based upon results obtained when the two are at the same temperature. There were therefore no data which would indicate whether it was the temperature of the metal or that of the gas which would be the more important factor in the reaction.

In the earlier experiments (Exp. 211) the rate of clean-up had appeared nearly independent of the temperature of the filament. At that time the effect of heating the bulb to 360° and of cooling it to -183° by immersing it in liquid air was tried, and it was found that the temperature of the bulb was entirely without effect. The value of ϵ obtained in these experiments was 0.0072 at a temperature of 1770° K with a filament having a surface of 0.126 sq. cm. When we found that these results were too low because of the resistance to diffusion in the tubing, it became necessary to test out the effect of the bulb temperature again with the new apparatus (Exp. 265). The bulb, however, in this case was so large that it was impracticable to cool it with liquid air, and we had to remain content with heating it to 300°. The results obtained in this way are given in Table II., Columns 3 and 5.

* Paper read before the New York Section of the American Chemical Society. From the *Journal of the American Chemical Society*, xxxv. No. 2.

It will be seen that raising the temperature of the oxygen around the filament from 25 to 300° makes no appreciable change in the value of ϵ .

This result is rather surprising. According to the ordinary conceptions of the mechanism of a chemical reaction, the effect of increasing temperature is somewhat as follows:—In order that a collision between two molecules may result in a chemical combination, the impact of the two molecules against each other must exceed a certain amount. At low temperatures no molecules, or only few, have velocities sufficient to produce strong enough impact. As the temperature rises the relative proportion of molecules which meet this requirement increases extremely rapidly, although still only a small proportion of the total number of collisions result in chemical action.

If the above theory is correct, one would expect that both the temperature of the oxygen and that of the tungsten would influence the rate of reaction. That the actual impact between such molecules would be very greatly affected by the temperature of the oxygen appears from the following considerations:—

Let us consider two molecules, one of molecular weight M_1 and the other of the weight M_2 . Let v_1 and v_2 be the velocities of these molecules, and T_1 and T_2 the temperatures corresponding to these velocities. Let us

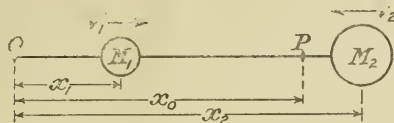


FIG. 3.

imagine these two molecules in the positions indicated in Fig. 3 moving towards each other with the velocities v_1 and v_2 . Let x_0 be the distance from O to P, the centre of gravity of the system of the two molecules. Let v_0 be the velocity with which P moves from O.

By the definition of centre of gravity, we have—

$$\frac{x_0 - x_1}{x_2 - x_0} = \frac{M_2}{M_1}$$

or—

$$\frac{x_0 - x_1}{x_2 - x_1} = \frac{M_2}{M_1 + M_2}$$

and for the corresponding velocities,—

$$\frac{v_0 - v_1}{-v_2 - v_1} = \frac{v_1 - v_0}{v_1 - v_2} = \frac{M_2}{M_1 + M_2} \quad (13).$$

Now, the impact with which they strike is proportional to the product of the mass of one of them by the velocity with which it approaches the common centre of gravity. That is, the impact is measured by $(v_1 - v_0)M_1$, but from (13) this gives for the impact I,—

$$I = \frac{M_1 M_2}{M_1 + M_2} (v_1 + v_2) \quad (14).$$

Neglecting constant factors, which would ultimately cancel out, we can place, according to the kinetic theory,—

$$T_1 = M_1 v_1^2 \text{ and } T_2 = M_2 v_2^2 \quad (15)$$

whence, combining with (14),—

$$I = \left(\sqrt{\frac{T_1}{M_1}} + \sqrt{\frac{T_2}{M_2}} \right) \frac{M_1 M_2}{M_1 + M_2} \quad (16).$$

What we now wish to find is the effect that will be produced by a change in the temperature of M_1 as compared with a change in temperature of M_2 . We obtain by differentiation—

$$dI = \frac{1}{2} \frac{M_1 M_2}{M_1 + M_2} \left(\frac{dT_1}{\sqrt{M_1 T_1}} + \frac{dT_2}{\sqrt{M_2 T_2}} \right) \quad (17).$$

If we represent by dT_1 and dT_2 the temperature changes

of M_1 and M_2 , respectively, which will change the impact by equal amounts, we get—

$$\frac{dT_1}{dT_2} = \sqrt{\frac{M_1 T_1}{M_2 T_2}} \quad (18).$$

Taking for oxygen, $M_1 = 32$, $T_1 = 298$, and for tungsten $M_2 = 184$, $T_2 = 1600$, we get—

$$dT_1/dT_2 = 1/5.5.$$

That is, raising the temperature of the oxygen 1° would increase the impact between the molecules as much as raising the temperature of the tungsten 5.5. From Table IV. we see that at 1600° the value of ϵ doubles in about 140° rise in temperature. Dividing this by 5.5, we see that raising the bulb temperature about 25° should double the value of ϵ if the rate of reaction is determined by the impact of the molecules. From Equation (16) it can be readily calculated that with the filament at 1600° the impact between oxygen molecules and tungsten atoms would be increased in the ratio 6.00 : 7.20 by raising the temperature of the oxygen from 25° to 300°. If the oxygen be maintained at 25° we find that to produce the same increase (*i.e.*, from 6.00 to 7.20) in impact by raising the temperature of the filament, it would be necessary to raise it from 1600° to 3160°. According to Table IV. we see that this would increase ϵ from 0.020 to about 0.200. Actually, however, we find no appreciable change in ϵ upon heating the bulb, and we must therefore conclude that it is *not* the impact of the oxygen molecules with the tungsten atoms which determines the rate of reaction.

According to the electron theory of metallic conduction of heat and electricity, metals contain free electrons which participate in the heat vibration, and have the same kinetic energy at a given temperature as the atoms of the metal. Oxygen, being an electro-negative element, easily takes up electrons, so it seems probable that an oxygen molecule would be more apt to take up an electron in striking the filament than it would to combine directly with the tungsten.

Let us consider this case from the view-point of the foregoing theory. That is, let us consider the impact of an oxygen molecule and a negative electron. We will place, therefore, in Equation (18)—

$$\begin{array}{ll} M_1 = 32 & T_1 = 298 \\ M_2 = 0.0005 & T_2 = 1600 \end{array}$$

Here, in place of $M_2 = 184$, we take $M_2 = 0.0005$, the "atomic weight" of an electron. Whence, from (18)

$$dT_1/dT_2 = 109.$$

This completely reverses the previous result, and we see that a change of 109° in the temperature of the oxygen would have no more effect on the amount of impact between the oxygen and the electrons than a change of only 1° in the temperature of the filament. In other words, if the first step in the reaction consists of a collision between an electron and an oxygen molecule, we would expect to find just what the present experiments have shown, namely, that the value of ϵ is not affected appreciably by changing the temperature of the bulb.

This hypothesis is an entirely reasonable one. We do not need to assume that the oxygen molecule takes up more than one electron to begin with, or that the oxygen molecule is dissociated or undergoes any other change. The taking up of a single negative charge would bring into play electrostatic forces tending to hold the molecule on the surface long enough for secondary reactions to occur. These may be, for example, the taking up of more electrons, the dissociation of the molecule into charged atoms, and the combination of these with each other and with tungsten atoms to form WO_3 . All these secondary reactions, however, would not influence the velocity of the reaction, since once an oxygen molecule was retained on the surface by taking up a single electron, there would then be ample time available for the subsequent changes.

On this hypothesis, the temperature coefficient of the reaction velocity may be due to two causes. First, the

increased velocity of the electrons at higher temperatures, which gives a higher percentage of them capable of giving sufficient impact to produce the reaction. Second, an increase in the number of free electrons at high temperatures might cause an increase in the reaction velocity with increasing temperature of the filament.

The electron theory seems to make it probable that the number of free electrons in a metal is very large, and that the number of them changes very little with increasing temperature (see Richardson, *Trans. Am. Electrochem.*, 1912, xxi., 69). Partly from this reason and partly because of the very high velocities of the electrons, it is probable that every oxygen molecule that strikes the filament is struck by many electrons, but is only capable of combining with those that happen to have an unusually high velocity.

There are other hypotheses, however, which may be advanced to explain the fact that ϵ is independent of the bulb temperature. We may assume, for example, that the surface of the metal is more or less completely covered with a film of oxide, through which the oxygen must diffuse before it can react with the metal. As the temperature of the metal increases, the oxide film would rapidly become thinner, and this fact would account for the increase in the rate of reaction as the temperature increases.

On this hypothesis, the oxygen would only react with the tungsten after it had diffused through the oxide film, and hence reached the same temperature as the metal. The temperature of the bulb in this case would naturally be without effect. Undoubtedly this sort of film plays an important part in gas reactions between solids and gases at atmospheric pressure (see, for example, Bodenstein and Fink, *Zeit. Phys. Chem.*, 1907, lx., 46), but it seems extremely improbable that such would be the case at very low pressures and at high temperatures. The strongest argument, however, against this theory is that the thickness of the film and hence the value of ϵ would vary with the pressure of the oxygen. This is, however, contrary to the results of the experiments. Another fact that indicates at least that any such film must be extremely thin is that the emissivity of the filament for both light and heat is entirely unaffected by the presence of oxygen (except below 1300°).

It must be pointed out that the reaction between oxygen and tungsten at low pressures obeys very simple laws, and does not appear to be sensitive to slight variations in the conditions. Reactions in heterogeneous systems at atmospheric pressure are usually enormously sensitive to catalytic disturbances and other irregularities which are probably characteristic of reactions that take place through an adsorbed film. Bodenstein's work on the reaction $2H_2 + O_2 = 2H_2O$ in contact with solid bodies is an example of this type of reaction. Another example is the contact process for SO_3 (see Bodenstein and Fink, *Zeit. Phys. Chem.*, 1907, lx., 1).

For all these reasons it would seem extremely improbable that there is any surface film which limits the rate of reaction. The theory that the oxygen reacts primarily with electrons in the metal is therefore made still more probable. It will be worth while to analyse the consequences of this theory more fully.

(To be continued).

Chloral-*p*-aminoazobenzene. — Mario Mayer. — Chloral-*p*-aminoazobenzene when prepared from chloral hydrate and *p*-aminoazobenzene is a dark red powder which dissolves in a mixture of benzene and petroleum ether (in the proportions 1 : 2). From the mixed solvents two different forms of the substance can be separated, one yellow fusing at 116°, and the other red fusing at 136°. The yellow form is converted into the red form at 120°. Chemically the two forms are identical. — *Atti della Reale Accademia dei Lincei*, xliii. [i.], No. 5.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

POSSIBLE CAUSE OF THE MIGRATION OF SALMON.

One of the most important problems of oceanography and biology is that of migrative fish. What cause guides them in their displacements and draws those that accomplish considerable voyages as do salmon? These fish often go up to rivers, and indeed go sometimes very far to milt. For this they leave the depths of the sea where they have grown up. We may then wonder what it is that incites them at the period of their reproduction to undertake a perilous peregrination. It has been said that they were carried away by the need of procuring for their eggs and for their future young fry, circumstances which alone allow of their development. But this finalist explication is open to much criticism. We must try and discover if this migrative phenomenon has no immediate determinism. M. Louis Roule, Professor at the Natural History Museum, has on this subject undertaken a series of studies, and in a paper presented before the Academy of Sciences by M. Edmond Perier, he exposes the first results at which he has arrived. He has effected his researches on the rivers of the Southern Brittany coast, and he has found that the proportion of oxygen dissolved in the water plays a very important rôle. According as this proportion is stronger or weaker the salmon go up the river or abstain from doing so. Salmon, doubtless like trout and other similar fish, have very intense respiratory needs, which are exaggerated at the period of reproduction. Consequently they only enter the rivers capable of satisfying these needs, thanks to the considerable amount of oxygen that their water holds in solution. Besides its scientific importance this conclusion presents an undeniable economical importance, for it will enable us to establish, thanks to a previous analysis, the list of river basins where trials of restocking will have some chance of success. It will no longer be sufficient to remove the young fry nor to construct costly ladders or scales, but one must know exactly the rivers where these works will be useful and those where they would have no effect.

NEW ARTIFICIAL MANURE.

For a long time it has been known that the nitrogen necessary to plants cannot be taken by them directly from the air. In 1886, on the roots of certain vegetable plants there was remarked the existence of large colonies of bacteria having the property of fixing the atmospheric nitrogen for the advantage of the plant on which they lived. So, then, we were in the presence of a kind of symbiosis. Great hopes were founded on these bacteria, for it was thought that the sowing of the land with these microbial cultures would considerably increase their cultural force. These hopes fell through, as did also those founded in 1901 on the azotobacter, the most powerful of the agents of nitrification. The question, however, has not been abandoned, and it would seem that a solution has been arrived at. It has been found, indeed, that turf treated in a special manner constitutes a particularly favourable environment for the growth of the azotobacter, and that the grounds manured with this turf show a very notable increase in their fertility. Before inoculating the turf with the microbe, it is necessary to transform it by the action of another microbe, so as to neutralise the humic acid it contains. The technic of the operation is then the following:—The raw turf, sown with the special microbe is kept during eight or ten days at a constant temperature, then sterilised by steam. It is then inoculated with a mixture of azotobacter and nitric bacilli. After a few days' incubation at a temperature of 26° it is ready to be employed. An interesting point to be noticed is that the azotobacter continues to develop in the soil, fixing new quantities of nitrogen. The results of the experiments of

culture are most encouraging. For the culture of potatoes, whilst farm-manure increases about 40 per cent the return per acre and artificial manures about 75 per cent, inoculated turf procures an increase in the return of 123 per cent. For carrots numerous correspondents are respectively 20, 28, and 260 per cent, for turnips 26, 47, and 100 per cent. If these results are confirmed by other experiments, and if this new produce for manuring suits all grounds, the manures of electricity will have a most serious rival to face, with whom they will have to undertake a very severe struggle.

SILICA FORMS THE HALF OF THE EARTH'S CRUST.

The terrestrial crust is formed especially of silica, and this fact is generally little known. It is because silicium and its derivatives are, for a reason unknown, the poor children of chemistry and mineralogy. In the treatises on chemistry employed in secondary education a small place is given to silica and to silicium, but the silicates are completely ignored. Prof. Henry Le Chatelier, Professor at the Sorbonne and Member of the Academy of Sciences, only explains this abstention of chemists by the somewhat routine respect of a too distant tradition. He has just put an end to these errors by giving to silica and to silicates the place that is their due. Silica is the most abundant of the chemical combinations existing in the crust of the earth. People have tried to form an idea of the average composition of the solid crust of our globe by making in different countries analyses of a very great number of rocks. Several thousands of samples have been taken, especially in the United States and in Norway. The results have been almost identical, and the corresponding figures may be corresponding figures may be considered as giving a pretty exact average for the whole world. The terrestrial crust thus contains 58.2 per cent of silica, 15.8 per cent of alumina, 7.1 per cent of oxides of iron, then some oxides of sodium, of potassium, of calcium, of magnesia, in proportions varying from 3.2 to 5.2 per cent. The crust of our globe contains also 1.5 per cent of water and 1 per cent of oxide of titanium. This silica is found partly in a state of free silica, often in a state of combined silica. The silicates are very numerous; feldspars, micas, pyroxenes form the principal families. Among the hydrated silicates we must mention, in the first place, clay, then compound silicate of iron, of magnesia, and of potash, constituting the green sand by which the artesian waters of Champagne and Normandy arrive in Paris. As to the industrial importance of silica it is immense. The silicated rocks, granites, porphyries, schists, &c., are employed as materials for building. The Vosges stones, which were used to build the Cathedral of Strasbourg, the mill-stone, a variety of chalcedony that is exploited in the neighbourhood of Paris, are likewise only silicates. The mill-stone, unalterable by the atmospheric agents and possessing the property of making one body with the cement, allows of the erection of buildings which are, so to say, indestructible. So it is employed systematically for the walls of prisons. Lastly, the ceramic industry, as well as the glass industry, are entirely based on the utilisation of siliceous matters. Glass, which is considered unalterable, is, on the contrary, very sensitive to the action of the temperature and of liquids. M. Henry Le Chatelier has particularly studied this important question of the chemical alterability of glass. The alteration of different glasses can sometimes be remarked without the employment of any precise measurement. Antique glass found in the soil shows an iridescent layer, superficial and deprived of transparency on account of the elimination of a part of the elements constituting the glass. This iridisation, which is so pretty, can, it is true, be produced artificially by heating during a few hours ordinary glass vases in chlorhydric acid diluted. Spherical bulbs thus treated have exactly the appearance of soap-bubbles. In other parts of the work Prof. Henry Le Chatelier studies the physical and optical properties of glass, metallic alkaline silicates, magnesias, and ceramic.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 7, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Some Calculations in Illustration of Fourier's Theorem." By LORD RAYLEIGH, O.M., F.R.S.

"Theory of Long Waves and Bores." By LORD RAYLEIGH, O.M., F.R.S.

"Protection from Lightning and the Range of Protection Afforded by Lightning Rods." By Sir JOSEPH LARMOR, F.R.S., and J. S. B. LARMOR, M.A.

On modern ionic views discharge in the atmosphere should originate at a place of maximum intensity of electric field and spread both ways from it along a line which should be roughly the line of force. The explanation of branching, zigzag, and multiple lightning discharges is to be sought on these lines. The introduction of a narrow linear conductor cannot sensibly disturb a steady field of force, and not at all if it is transverse to the field. Thus it would seem to be the top of the building itself, not of the lightning conductor, that attracts the discharge, and the function of a single rod can only be to lead it more safely away. But a number of rods distributed over the area of the roof, and effectively connected to earth by a conductor, can, by their joint action, lift the intensest part of the field from the top of the building to the region around their summits, and so obviate or much mitigate the danger of discharge from above to the building which they cover. In illustration, diagrams are given of a vertical field of force as disturbed by vertical pillars of semi-ellipsoidal form and of various breadths, or by an earthed conducting region overhead such as might be originated by gradual discharge from a pointed rod.

"Newcomb's Method of Investigating Periodicities and its Application to Brückner's Weather Cycle." By Prof. A. SCHUSTER, Sec. R.S.

"Flow in Metals Subjected to Large Constant Stresses." By E. N. DA C. ANDRADE.

The law connecting the extension with time for wires of various metals subjected to large stresses has been examined at different temperatures. The stress was kept constant throughout the flow by the device of a hyperbolic weight employed in former experiments. The different types of flow observed for different metals at room temperature are only particular cases of one general law governing the flow of all single metals, and can all be found for one metal by choosing an appropriate temperature; thus, soft iron at 450° C. behaves similarly to lead at 15° C. The formula $l = l_0(1 + \beta t^{1/3})e^{\kappa t}$ can be made to represent the increase of length l with time t in all cases by suitable choice of the constants l_0 , β , κ . The viscous part of the flow, expressed by κ , does not exist at low temperatures, but becomes more and more predominant with rise of temperature. The distinction of the viscous part of the flow from the initial part of the flow, and the behaviour in general, can be explained from the co-existence of the crystalline and the amorphous state in the metal.

The behaviour of wires of solid distilled mercury shows that the rapid initial flow characteristic of the single metals is not due to impurities.

Duplex alloys behave altogether differently to the single metals with respect to the flow, the anomalous behaviour corresponding to a difference in type of crystalline structure.

"Eddy Motion in the Atmosphere." By G. I. TAYLOR.

The paper contains a theoretical discussion of the function of eddies in conveying heat and momentum through a fluid. It is shown also that measurements of the temperature of the air over the Great Bank of Newfoundland made

by the author last year, lead to the conclusion that eddies extend upwards over the sea to a height of at least 800 metres; and that there is no appreciable diminution in their size or intensity in this height.

On the assumption of a uniform amount of eddy motion, the velocity of the wind at various heights above the ground is calculated, and shown to agree with the most recent observations carried out over Salisbury Plain. The actual amount of eddy motion is calculated both from wind velocity and from temperature measurements, and the two values are found to agree within the limits of error. This tends to confirm a general theorem about eddy motion in two dimensions which is deduced from theoretical considerations.

"Properties of Magnetically-shielded Iron as Affected by Temperature." By Prof. ERNEST WILSON.

In a paper recently read before the Royal Society, it is shown that if stalloy in ring form is shielded from the earth's magnetism and subjected to a considerable magnetising force at atmospheric temperature, the permeability can be increased. The present experiments deal with the effect of allowing stalloy to cool down through the temperature at which it regains magnetic quality when in a shield and when under the influence of a magnetising force due to a continuous current. Two specimens have been subjected to this treatment, and in each case the maximum permeability has a value of over 10,000 when the specimen is at atmospheric temperature. The dissipation of energy by magnetic hysteresis for a given value of the magnetic induction is reduced by the treatment.

ROYAL SOCIETY CONVERSAZIONE.

THE Royal Society Conversazione, held on Wednesday, May 13th, at the Rooms in Burlington House, was quite up to its usual level of interest.

Short demonstrations were given during the evening by Prof. J. P. HILL, F.R.S., on the Percy Sladen Expedition to Brazil, 1913, illustrated by numerous lantern slides and views of the regions visited. Also by Mons. P. SCHILOWSKY, upon The Application of Gyroscopes to the Three Systems of Locomotion; on land, on sea, and in the air. Gyroscopes with models of monorail cars, ships, and aeroplanes were used to illustrate the lecture.

Among the more striking exhibits were the following:—

Mr. C. R. DARLING. Some New Surface Tension Phenomena, and an Experiment to Show the Structure of Liquid Jets.

A globule of oil was formed on the surface of water, and a drop of quinoline allowed to fall upon it. On this drop reaching the oil-water interface, the globule burst with considerable violence. Orthotoluidine globules were formed on a water surface, and a large globule of dimethyl-aniline was added, which then proceeded to absorb the orthotoluidine. The process of absorption resembled the feeding of certain lower organisms. The experiments were made visible to the audience by projection upon a screen and the extraordinary motions due chiefly to surface tension were watched with considerable interest.

Prof. LEONARD HILL, F.R.S., and Mr. O. W. GRIFFITH. The Calceometer.

The calceometer is an instrument designed to measure the degree of comfort in a room, or a public hall, or a factory, in so far as that depends on the rate of cooling of the human body. Comfortable conditions are indicated by gentle oscillations of the pointer—about a mean value of 30 calories per minute. A low steady reading denotes monotony and oppressiveness; violent oscillations about a high mean value are evidence of excessive cooling by an unpleasant draught.

Mr. W. A. DOUGLAS RUDGE. Electrification produced during the Raising of a Cloud of Dust.

A delicate electroscope was attached to a metallic rod

tipped with radium, which ionised the air in the neighbourhood. The electrification caused by blowing dust out of a bottle was indicated by the charging of the electroscope. Dust of an acidic nature, silica, or molybdic acid gave a negative charge, while metallic oxides and organic bases gave a positive charge.

Mr. C. V. BOYS, F.R.S. Blower for very Large Soap Bubbles.

The difficulties of blowing and detaching very large soap bubbles were overcome by a special form of injector blow-pipe swivelled at right angles to its length about the injector nozzle as an axis, and with a diverging cone of flexible fabric with a serrated edge, made impervious to liquid a short distance behind the serrations. This cone was kept open by two springs. The absorbent material, up to the impervious band, provided liquid sufficient for a large thin bubble, but not so much as to make it unduly thick, for the limit of possible diameter of a bubble is greater as its thickness is less, and the points of the serrations feed the bubble in numerous very fine streams. Bubbles 3 or 4 feet in diameter are possible, and by injecting a little warm air during their formation they can be made to rise and they then form magnificent objects.

Mr. LOUIS BRENNAN, C.B. The Iridoscope.

A device by which it is possible to make a large sheet of soap film. By standing the frame holding this film upright in a suitable light fine displays of colour are produced by the natural thinning of the upper portion of the film, or by playing upon it by a jet of air.

Mr. W. DUDELL, F.R.S. Water Model of the Electric Arc.

The model exhibited consisted of a mushroom valve. The pressure tending to reseal the valve was so arranged that it diminished very rapidly as the valve lifted. In this way, when the flow of water was increased through the valve, the difference of pressure between its two sides decreased and thus represented one of the properties of the electric arc. When a steady flow was established and a column of water having a definite periodic time connected to the valve oscillations were set up similar to those obtained with an electric arc.

THE SILICA SYNDICATE, LTD. Some New Developments in the Manufacture of Apparatus in Transparent Quartz Glass.

The Silica Syndicate had a large number of exhibits. A great advance has recently been made by the invention of a method of making an air-tight seal between quartz glass and metal, which consists essentially in flowing pure lead into the hot quartz tube in a vacuum; the metal makes perfect contact with the quartz, and vacuum apparatus of all descriptions can be constructed in this way. Electric lamps, X ray tubes, electric radiators, and other apparatus to which the lead seal was successfully applied were shown.

THE POLYCHROMIDE COMPANY (THE DOVER STREET STUDIOS, LTD.). Instantaneous Photographs on Paper Taken in Natural Colour by the Polychromide System.

The optical separation of the natural colour of the object photographed is accomplished by means of the Hamburger-Conrady colour separation camera, which exposes three plates simultaneously—representing the red, yellow, and blue sensations in the superposed positives on gelatin-silver emulsions, which constitute the complete colour records exhibited. A very fine collection of photographs were shown, including one of the President of the Society; the colour rendering was excellent, and the exhibit caused great interest.

THE BRITISH MUSEUM (NATURAL HISTORY). A Selection of the Specimens Collected on the British Antarctic ("Terra Nova") Expedition, 1910–1913, under the Leadership of the late Capt. R. F. Scott, C.V.O., R.N.

Mr. F. W. ASTON. A Simple Microbalance for the Determination of the Densities of Small Quantities of Gases.

The balance was made entirely of fused quartz, and consisted of a beam of the simplest possible construction, bearing at one end a small closed bulb and at the other a solid counterpoise. The whole was supported by a knife edge working on a polished quartz plate, and enclosed in a small case made of plates of glass in such a way that the pressure could be varied at will. The capacity of the whole "case" was about 2 cc., and the movement of the balance could be watched through a small telescope. It was sensitive to about one-millionth of a mgrm.

Mr. ROLLO APPELYARD. Chain Apparatus for the Approximate Measurement of Logarithmic and Hyperbolic Functions.

The apparatus consists of a chain suspended so as to form one-half of a true catenary, and it is shown that by suitably proportioning the scale of measurement to the tensions of the chain the various quantities required can be obtained, to a first degree of approximation, by direct measurement from the suspended chain. These quantities include (1) the base of the Napierian logarithms; (2) the anti-logarithms of numbers to the Napierian base; (3) the hyperbolic function, $\sin x$, $\cos x$, $\tan x$, and $\sec x$. Special interest attaches to the apparatus, as it is just 300 years since the invention of logarithms by Baron John Napier, of Merchiston.

Prof. A. W. BICKERTON. The Polyscope.

A kaleidoscope rendered so optically perfect that a hundred reflections of a point or object may be seen. The angles of one are 30° , 60° , and 90° . Of the other, two angles 45° and one of 90° . They produce two classes of patterns, one suitable for textile fabrics, cretonnes, &c., the other suitable for floor cloths, tiles, &c.

Messrs. CHANCE BROTHERS AND CO., LTD., showed a number of specimens of Glass for Making Spectacle Lenses for the Absorption of Ultra-violet and Infra-red Rays and for the Reduction of Glare, based on experimental results given in Sir William Crookes's recent paper read before the Royal Society. Some of these glasses have the valuable property of almost completely absorbing the heat and ultra-violet radiations, and are useful for many purposes besides spectacles.

Exhibits were also given by the MARINE BIOLOGICAL ASSOCIATION, Profs. MACBRIDE, A. F. STANLEY KENT, E. B. PAULTON, the ASTRONOMER ROYAL, and many others.

PHYSICAL SOCIETY.

Ordinary Meeting, May 8, 1914.

Dr. A. RUSSELL, Vice-President, in the Chair.

A PAPER entitled "*Some Gyrostatic Devices for the Control of Moving Bodies*" was read by Dr. J. G. GRAY.

The paper dealt with a number of new contrivances for stabilising, steering, and forcibly manoeuvring moving bodies, such as torpedoes and airships.

A number of old experiments were first shown. These included the "gyrostat on stilts" and "gyrostat on gimbals" experiments due to Lord Kelvin, the "crossed bifilar" experiment due to Prof. Blackburn, and a stilt top devised by Prof. Harold Wilson. It was shown that the gyrostatic system in each of these experiments, although exhibiting considerable balancing power, was not possessed of real stability. An unstable body rendered truly stable by gyrostatic action must possess the property that if displaced from the mean position it returns to, and comes to rest in, that position. The mean position is that in which the potential energy of the gyrostatic system is a maximum, and if the system is disturbed energy must be supplied to restore it to the mean, or undisturbed, position.

A number of new gyrostatic models were displayed in action. These include two-wheeled and four-wheeled gyrostatic motor cars and bicycles. These all provide examples

of gyrostatic systems provided with complete or real stability, and in all the cases shown the stabilising forces are derived from the propelling system.

One of the cars shown runs on two wheels in tandem, and is stabilised by a single gyrostat. This gyrostat is mounted in the car and controls the steering mechanism; it forms, in fact, a gyrostatic chauffeur. The model illustrated a new form of torpedo and airship control.

A second form of motor car, which also runs on two wheels in tandem, consists of two parts, a front one and an after one. The front part carries a gyrostat, the back part the propelling mechanism, and the two parts are connected together by means of a vertical hinge. The front part is propelled by the back part, and the arrangement is one of complete stability. The entire system may be manoeuvred by means of the gyrostat. It was pointed out that by properly fitting an airship with a gyrostatic "nose" it should be possible to manoeuvre forcibly the airship by means of forces derived from the propellers.

The bicycles, which are provided with gyrostatic riders, are examples of moving bodies steered by gyrostatic action. The action is quite different from that of an ordinary bicycle. They are not "momentum" instruments.

The devices shown are at once applicable to long-distance torpedoes, both submarine and aerial. The gyrostatic system may be operated by the wireless transmission of electrical action.

At the conclusion of the paper the author showed a new series of animated gyrostats.

DISCUSSION.

Dr. W. WATSON thought the mechanisms shown were of great theoretical importance. He gathered, however, that the author himself thought they were more of theoretical than practical interest. He concluded some time ago that a two-wheeled car would not be of much use, as, although gyrostatic control worked satisfactorily either on a straight path or on a curved path of constant curvature, any attempt to alter the curvature had to be made with great caution. Hence a train built on this system would have to slow up on approaching either the beginning or the end of a bend. With a motor car, where one had to steer immediate courses on account of other traffic, the arrangement would be impracticable. At one time, when some cars had engines laid longitudinally and others transversely, makers of the latter type claimed that gyrostatic action came into play and tended to prevent skidding. However, unless the gyrostat was free to move relatively to the car, one might as well have a lump of iron in its stead. He had investigated the amount of relative motion which might take place due to give in the springs or mountings, and it was quite insufficient to allow of appreciable gyrostatic action.

Mr. DUDELL complimented the author on the collection of beautiful models which he had brought before the Society and the admirable way in which he had explained the principles underlying their action. He asked what speed was attained by the flywheels of the gyrostats.

Mr. R. S. WHIPPLE also expressed his admiration of the models.

Mr. F. J. WHIPPLE asked if the author had worked out the theory of the ordinary bicycle, and if it was his considered opinion that the rider had to perform the actions which he had described in steering. It was his opinion that when travelling rapidly this was not so; and that there was a stabilising effect due to the gyrostatic action of the front wheel. This was particularly noticeable in the way in which the wheel seemed to be pulled back into position if, when riding without the hands, the cyclist encountered a small stone.

Dr. RUSSELL asked concerning the use of the word "gyrostat." He remembered on one occasion when Lord Kelvin was showing some of these experiments to von Helmholtz an accident occurred which resulted in one of the gyroscope wheels passing through Helmholtz's silk hat. After that it was customary to enclose the gyroscope

in a brass case, and it was then usually called a gyrostatt. He did not quite see why.

The AUTHOR, in reply, said that the larger gyrostatts could be taken up to a speed of 20,000 revs. per min. in half-a-minute, and would run for 75 minutes. In steering a bicycle the rider turns the front wheel to the side to which the machine leans, and the forward momentum brings it up to the vertical position. The gyrostatic action helps, but only to a very slight extent. The name "gyrostat" was the one invariably used at Glasgow since Lord Kelvin's time.

A paper entitled "*A Graphic Treatment of Cusped Wave-fronts, and of the Rainbow*," by Mr. W. R. BOWER, was taken as read in the absence of the author.

A method of drawing the cusped wave-fronts produced by refraction and reflection at a spherical surface and a graphic treatment of the elementary theory of the rainbow are described in the paper. The method is based upon the properties of the centre of junction. In the case of reflection at a spherical surface in which aplanatic points are not available the position of the junction centre is obtained by elementary geometry.

By the use of junction-centres the distribution of the successive foci obtained on refraction and reflection at a spherical surface is readily plotted. If in the case of a rainbow it is assumed that the emergent portion of the effective pencil, as well as the incident portion, is one of parallel rays, then the distribution of foci with regard to the drop is a symmetrical one.

The caustics on refraction and reflection are also readily drawn as loci of points and envelopes of rays. Hence the wave-surfaces can be obtained. These in some regions are cusped, and the caustics are the loci of the cusps.

In the case of pencils that are effective in producing rainbows, the lengths of the incident portion of the chief ray intercepted by the spherical drop of radius, r , and a concentric sphere of radius, $r\mu$, are in the ratio 1 to $n+1$, where n is the number of internal reflections. This leads to a geometrical construction for finding the points of incidence of the chief rays of the effective pencils. These rays are at minimum deviation, and the same chief ray remains at minimum deviation, although the associated pencil may be converging or diverging.

SOCIETY OF CHEMICAL INDUSTRY. (LONDON SECTION).

Ordinary Meeting, May 4, 1914.

Prof. W. R. E. HODGKINSON in the Chair.

The following papers were read and discussed:—

"*A Reaction of Tetranitromethane*." By W. R. E. HODGKINSON.

The author describes a solvent action in certain metals, i.e., such as form amides or amino-like compounds, of an alcoholic ammoniacal solution of tetranitromethane. When the metal is placed in such a solution a yellow colour develops, the temperature rises, and there is a slight gas evolution ($N_2(CO_2)$). The action only becomes vigorous with copper after a small quantity of the blue cupramine compound has formed. When a cupramine solution is added to an alcoholic solution of tetranitromethane crystals form rapidly. They are identical with those formed from the metal. Similar results were obtained with nickel, zinc, cadmium-amine solutions, and with ammonium double salts of the metals. The salts appear to be of the general type $C(NO_2)_3 \cdot NHM'_3 \cdot NH_3$. They are nearly all deliquescent, and when rapidly heated explode.

"*Application of Jets for Mixing*." By Dr. OSCAR NAGEL.

The low efficiency of jets is caused by the fact that about 75 per cent of the energy is consumed in the whirl which

is formed in the transit of the jet from one nozzle to another. This whirl effects the most intimate mixture of the motor-jet with the medium to be moved.

The use of jets as mixers is therefore suggested for various operations, such as the chamber process of manufacture of sulphuric acid. Preliminary experiments in this direction have been successful.

"*Apparatus for the Automatic Measuring and Injection of Chemicals*." By the Hon. R. C. PARSONS, M.A., M.Inst.C.E.

The author having referred to the crude methods generally adopted for introducing chemicals into water previous to its being filtered, proceeded to describe his low pressure injector, known by the name of the "Tiltometre," which is operated by means of the pressure obtained by inserting a venturi tube into the main in which the water to be treated flows. He then gave the results of the tests of this instrument, which proved to be an accurate and reliable apparatus for automatically treating water with a constant percentage of chemical, although the flow varies considerably.

He next explained his "High Pressure Chemical Injector," which also works by means of the pressure derived from a venturi tube inserted in a main.

This apparatus can inject against any pressure, and consists of two cylinders in which pistons having wide circumferential grooves move quite freely, and by means of a controlling valve are made to eject the chemical alternately, thus maintaining a regular flow. Above the cylinders are the inlet and outlet valves, the former for admitting the chemical from a tank in which it is stored, and the latter through which it is injected into the main. One side of this instrument is a manometer for indicating the venturi pressure due to the flow through the main, and on the opposite another manometer attached to a small venturi tube through which the chemical ejected passes, and the amount discharged measured. The ratio of these discharges gives the percentage of chemical added, and can be adjusted by the regulating valve.

Both these instruments are shown to be simple, durable, reliable, and to yield very accurate results.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, May 6, 1914.

Mr. A. CHASTON CHAPMAN, President, in the Chair.

MESSRS. Lauchlan Henry Dyke Acland, Walter Alan Gibbings, Frederic Herbert Lees, and William Henry Woodcock were elected Members of the Society.

Certificates were read for the first time in favour of Messrs. William Roscoe Hardwick, B.Sc., F.I.C., 13, Batavia Buildings, Hackney, Hey, Liverpool; Harold Fletcher Hills, F.C.S., Commercial Gas Works, Stepney, E.; Robert Hindle Kay, 72, Manor Road, Stoke Newington, N.

"*Detection of Castor Seeds*." By G. D. LANDER and J. J. GEAKE.

A modification of the precipitin reaction as practised by Mooser and others, whereby direct extraction of a suspected material by means of physiological saline replaces the more costly and tedious method of extraction by glycerol.

"*Composition of Milk and Milk Products*." By H. DROOP RICHMOND.

As in previous years, the author gave a summary of the results of the analyses made in the Aylesbury Dairy Co., Ltd., during 1913; a sample of goat's milk and one of human milk was examined. It was shown that the aldehyde figure of cream calculated on the portion free from fat was the same as that of milk.

"Note on 'Sharps'." By J. F. LIVERSEEGE and G. D. ELSDON.

The permissible percentage of calcium sulphate in "sharps" (from grain) was discussed and a series of analyses of known samples was given.

"Action of Weak Acids on Soluble Fluorides." By P. A. ELLIS RICHARDS, F.I.C.

The author shows that the fluorides of the alkali metals are decomposed by many organic acids, including acetic, formic, tartaric, malic, lactic, benzoic, and salicylic acids, with liberation of hydrogen fluoride. Carbon dioxide gas passed through a solution of either sodium or potassium fluoride has a similar action.

"Simple Form of Fat Extractor." By G. A. STOKES.

A simple fat extraction apparatus can be constructed by suspending a fat-free extracting thimble by means of wire in a long necked conical flask. The wire is fixed, and can be raised and lowered in the stopper, in which a condenser is fitted in the usual way.

INSTITUTE OF METALS.

MAY LECTURE.

THE annual May lecture of the Institute of Metals was delivered by Prof. E. HEYN, of Berlin, in the evening of Tuesday, May 12th, at the Institution of Chemical Engineers, Engineer Vice-Admiral Sir HENRY J. ORAM, K.C.B., F.R.S., President of the Institute of Metals, being in the Chair.

Prof. HEYN said that it was a well-known fact that the welfare and convenience of modern mankind was, to a very considerable extent, influenced by the achievements of the engineer. People admired his work, and were daily confiding life and health to his creations. But only few were conscious of the fact that engineering work was, to a great amount, dependent on the possibility of manufacturing sound materials fit for the purpose and of keeping them sound in the course of the manifold processes that these materials required to go through until they were assembled into the admirable engineering structures presenting themselves to the public eye. Few persons were conscious of the enormous amount of thought bestowed on the question of soundness of materials by thousands of men fighting continuous struggles against the numerous hidden dangers involved in the intricacy of structural material and working strenuously towards its perfection and reliability.

Certain structural members might fail even without being subjected to stresses in service. For instance, it had often been observed that condenser tubes made out of brass cracked simply when stored up in the yard. Some articles made out of this metal, when exposed to atmospheric influences, underwent an alteration to such an extent that they might be crumbled between the fingers. Similar phenomena could be stated in structural members made out of other metals and alloys, when they were manufactured under unfavourable conditions, which lead to serious internal strains.

The author said that he had made a special study of the phenomena connected with internal strains, investigating their causes and devising a method for measuring their amount. In his lecture the author dealt specially with the internal strains produced by cold working of metals (cold drawing, cold rolling, cold hammering, &c.). He showed that by these operations under unfavourable conditions internal strains might be set up in structural members which came close to their resisting power, so that even trifling additional strains caused by external forces or other circumstances (scratching of the surface, unequal heating or cooling, slight corrosion by certain agents, which were contained in the atmosphere or by certain paints) might lead to unforeseen fracture. He discussed the means for removing or diminishing such dangerous internal strains, and illustrated his lecture by numerous samples taken from the domain of practical engineering.

NOTICES OF BOOKS.

The Synthetic Use of Metals in Organic Chemistry. By ARTHUR J. HALE, B.Sc.(Lond.), A.I.C. London: J. and A. Churchill. 1914.

FOR advanced students of organic chemistry this will be found a very useful handbook. The different types of reactions effected by the metals and their salts are described, with references to the original papers relating to them, and full directions are given for practical work illustrating some of the more important reactions. The student who has a fair general knowledge of the operations of practical chemistry will be quite well able to carry out the experiments without any help from a demonstrator, for the directions are very explicit, and quantities employed and yields to be expected are always stated. For the chapters on practical work, which form perhaps the most useful part of the book, the information has been collected from many foreign periodicals, and it will be a boon to students who do not read German and French easily, or to those who cannot readily get access to the *Berichte*, &c.

A Third Year Course of Organic Chemistry. By T. P. HILDITCH, D.Sc.(Lond.), F.I.C. London: Methuen and Co., Ltd. 1914.

THIS book is the sequel to Dr. Dunstan's "First Year Organic Chemistry" and Mr. F. P. Thole's "Second Year Organic Chemistry," and deals with the heterocyclic compounds, and also with some of the more complex aliphatic and carbocyclic compounds not discussed in the earlier books. These include the sugars, polypeptides, and terpenes. The book will be found a useful and safe guide for candidates for such examinations as the Honours B.Sc. degree of London University. The author has introduced many valuable summaries and schemes showing constitutions, which are likely to impress themselves on the student's memory, and he has been judicious in selecting his material well, and not overburdening the text with details. It is a pity that small print has been used so much, for the type in which some of the formulæ are printed renders them almost undecipherable.

Karbid und Silizide. ("Carbides and Silicides"). By Prof. Dr. OTTO HÖNIGSCHMID. Halle-a.-S: Wilhelm Knapp. 1914. (Mk. 13.60).

THIS monograph treats from a scientific point of view of the binary compounds of carbon and silicon with other elements, and gives a very complete account of the subject. Technical processes and patents are not, as a rule, included for discussion, but all laboratory work on carbides and silicides is very fully described. The early sections deal with the preparation and properties of carbides in general, and then each individual compound is described in full. The silicides are treated similarly, and the monograph concludes with an appendix contributed by Dr. Otto Flaschner on the thermic analysis of silicides and carbides.

Contribución al Estudio de la Imagen Latente Fotografica. ("Contribution to the Study of the Photographic Latent Image"). By LUIS GUGLIAMELLI. San Martin: Imprenta de "El Nacional." 1913.

THIS volume contains a thesis presented to the University of Buenos Aires by the author for his doctorate. It gives a critical summary of the various hypotheses concerning the latent image which have been put forward, grouping them as physical, chemical, and physico-chemical. The last class, and in particular the colloidal theory, is considered in the greatest detail, the author believing that the bulk of the evidence that has been accumulated is in its favour.

CORRESPONDENCE.

WEBSTER FUND.

To the Editor of the Chemical News.

SIR,—Will you kindly allow me to announce through your columns that the fund subscribed in 1910 on an appeal for which I made myself responsible, and devoted to the relief of Mr. Charles S. S. Webster, of Bristol, research chemist, is now exhausted. Some £200 was raised, and paid into an account at the London County and Westminster Bank, Bayswater Branch. After providing for immediate necessities, the remainder (£150) has been paid over in monthly payments of £4. The situation of the family is still one of the greatest necessity, and if any of your readers would subscribe a further amount it will be dealt with in the same way. On a first appeal I have a promise of an annual payment of £10 over a period of three years.

Communications to the undersigned, or cheques made payable to the Manager, London County and Westminster Bank, Bayswater Branch, and crossed C. S. S. Webster Fund.—Yours, &c.,

C. F. CROSS.

4, New Court, London, W.C.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvii., No. 5, 1914.

Active Modification of Nitrogen.—H. B. Baker and R. J. Strutt.—Tiede and Domcke have stated that the luminescence of active nitrogen is not observed if the gas is absolutely free from oxygen. The authors, however, find that this is not the case. They point out that the luminescence has never been put forward as a proof of the presence of active nitrogen, but that the ground for the conclusion that an active modification is present is the formation of hydrocyanic acid, for example, when the gas from a vacuum tube is led through organic compounds containing hydrogen. The luminescence appears in nitrogen which has been exposed to the action of phosphorus (thus removing all oxygen) for a long time, and the nitrogen evolved from potassium nitride also gives it.

Hypoborates from Gaseous Boron Hydrides and Bases.—Alfred Stock and Ernst Kuss.— B_4H_{10} and B_2H_6 give the same substance when they react with alkalis. In each case hypoborates are formed, the reactions being $B_2H_6 + 2KOH = 2KOBH_3 + H_2$, and $B_4H_{10} + 4KOH = 4KOBH_3 + H_2$. $KOBH_3$ is hygroscopic, hydrogen being evolved at the temperature of the room. $KOBH_3 + H_2O = KBO_2 + 5H$. Alcohol dissolves the hypoborate, which undergoes partial decomposition. Acids, especially acetic acid, decompose the salt or its solution simultaneously. $KOBH_3 + HCl + 2H_2O = H_3BO_3 + KCl + 5H$. With solutions of nickel salts a black insoluble nickel boride, Ni_2B , is obtained. When potassium hypoborate is heated to about 500° it loses a large part of its potassium in the metallic form.

New Type of Complex Tungsten and Molybdenum Cyanides.—Oscar Olsson.—A series of complex cyanides of tetravalent tungsten which are analogous to the molybdenum cyanides of the type $Me_4Mo(CN)_8 \cdot xH_2O$, can be obtained from $K_3W_2Cl_9$. Where these compounds are titrated with potassium permanganate they are not converted into tungstic acid but into complex pentavalent tungsten cyanides of the general type $Me_3W(CN)_8 \cdot xH_2O$. It is probable that the anomaly in the valency determination of molybdenum with permanganate in the complex cyanides of the type $Me_4Mo(CN)_8 \cdot xH_2O$ is to be ascribed to the formation of pentavalent complex molybdenum cyanides, and that the compounds $Me_4Mo(CN)_8 \cdot xH_2O$ are to be regarded as derivatives of tetravalent molybdenum.

Atti della Reale Accademia dei Lincei.

Vol. xxiii. [i.], No. 5, 1914.

Oximes of α -Naphthylphenyl Ketone.—Mario Betti and Pasquale Poccianti.— α -Naphthylphenyl ketone, $C_{10}H_7 \cdot CO \cdot C_6H_5$, being an asymmetrical ketone should give two isomeric oximes. By the action of hydroxylamine upon α -naphthylphenyl ketone the authors have obtained a mixed product with no sharp melting-point, which when re-crystallised from alcohol gives a compound of constant melting-point and uniform aspect. If hydroxylamine liberated from its chlorhydrate by means of alkali is used, the product is chiefly the isomer which melts at 127° , but if the chlorhydrate is used with no alkali the other isomer, melting at 161° , predominates. A mixture of equal quantities of the two compounds melts at 135 – 140° , and a mixture of two parts of the 161° compound with one of the 127° compound melts at 140 – 145° , and it is possible that the mixture is the oxime (m. p. 140 – 142°) described by Kegel. When the 127° compound is dissolved in ordinary alcohol acidified with dilute hydrochloric acid it is transformed into the 161° compound. The same transformation also takes place spontaneously.

MISCELLANEOUS.

Association of Teachers in Technical Institutions.—The Association of Teachers in Technical Institutions will hold its Eighth Annual Conference at Liverpool during Whitsuntide, May 30 to June 3. The educational meetings will be held in the Large Hall of the Central Municipal Technical School. This Association is the only representative body of Technical Teachers in the kingdom, and its Conferences are therefore of considerable importance in the educational world. The open meetings begin on Monday, June 1, at 10.30 a.m., when the Chairman of the Liverpool Education Committee, Councillor J. W. Alsop, B.A., J.P., will welcome the Conference to Liverpool, and the President, Mr. P. Abbott, B.A., will deliver his Presidential Address. During the Conference papers will be read by Mr. W. Hewitt, B.Sc., the Director of Technical Education for Liverpool, Prof. Haldane Gee, Mr. W. E. Harrison, Mr. Laurence Small, Mr. W. R. Bower, and others. Sectional meetings will be held on the afternoon of June 2, when papers of special interest to the various sections of Technical Education will be read. Resolutions on matters of educational and professional interest will be discussed at the various meetings. The Annual Dinner will be held at the Exchange Station Hotel on the evening of June 1. Visits to Port Sunlight and Messrs. Cammell Laird and Co.'s works, and a reception by the Lord Mayor at the Town Hall, are amongst the many social items which have been arranged by the Conference Committee, and an Exhibition of Books and Scientific Apparatus will be held throughout the Conference at the Technical School.—J. PALEY YORKE, Hon. Secretary, 55, Fife Avenue, Upper Clapton, N.

MEETINGS FOR THE WEEK.

TUESDAY, 26th.—Royal Institution, 3. "Natural History in the Classics," by Prof. D'Arcy W. Thompson C.B.

THURSDAY, 28th.—Royal Institution, 3. "Identity of Laws, in General and Biological Chemistry," by Prof. Svante Arrhenius, D.Sc., &c.

Royal Society. "Studies of the Processes Operative in Solutions—XXIX., The Disturbance of the Equilibrium in Solutions by 'Strong' and 'Weak' Interfering Agents," by H. E. Armstrong, and E. E. Walker. "Type-reading Optophone," by E. E. Fournier d'Albe. "An Application of an Electrolytically-produced Luminosity forming a step towards Telectroscopy," by L. H. Walter. "Convection of Heat from Small Cylinders in a Stream of Fluid and the Determination of the Convection Constants of small Platinum Wires with applications to Hot-wire Anemometry," by L. V. King.

FRIDAY, 29th.—Royal Institution, 9. "Plant Autographs and their Revelations," by Prof. J. C. Bose, M.A.

SATURDAY, 30th.—Royal Institution, 3. "Fiords and their Origin," by Prof. J. W. Gregory, F.R.S., &c.

THE CHEMICAL NEWS

VOL. CIX., No. 2844.

AN IMPROVED SULPHURETTED HYDROGEN APPARATUS.

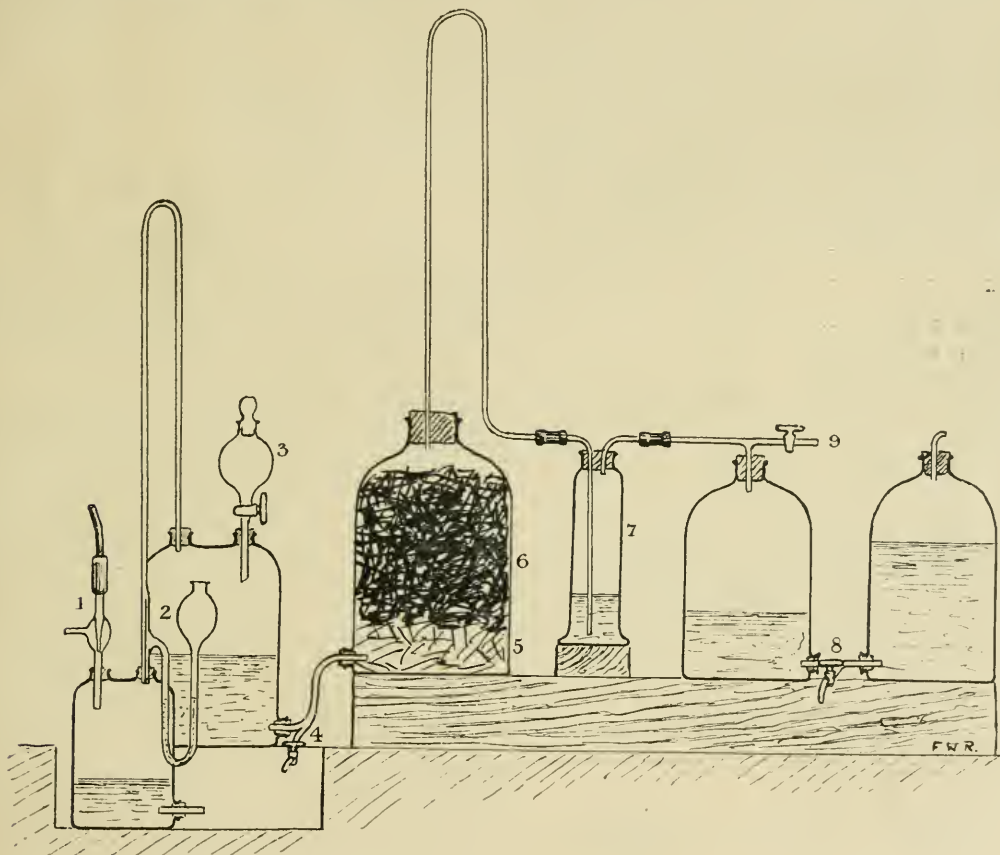
By FREDERIC WILLIAM RIXON.

THE apparatus described below has undergone a severe test for six months; during that time it has worked most satisfactorily. It possesses certain advantages which will

of water in this tube regulates the pressure of gas given by the apparatus.

The air pressure forces acid through the wide tube (4) on to the sulphide (6), a layer of coarsely broken glass (5) acting as a rough filter. The gas is washed (7) and delivered at the tap (9) or stored in the vessels (8), from which the solution may be taken. A tap between 6 and 7 may prove a convenience.

Renewal of acid follows by means of funnel (3) and tap (4). The whole apparatus may be readily fitted up from stock material, and admits of considerable variation to meet different requirements; for large laboratories it can be made to act automatically and deliver gas at a constant pressure, while if occasional supply only is required the apparatus will stand idle without losing efficiency.



be equally appreciated in laboratories where sulphuretted hydrogen is used constantly or even very intermittently. Some of these advantages may be mentioned.

A larger charge of iron sulphide may be used; the spent acid is easily replaced; when the apparatus is not in use the acid cannot possibly come into contact with the sulphide; the acid is totally enclosed; there is a reservoir of gas; gas and solution can be obtained, and the arrangement is practically fool proof.

Description of Apparatus.

Air pressure is obtained by using a filter pump (1) as a blower; too great pressure is relieved by the safety tube (2), which is of wide tubing sealed with water; the height

The only replacement entailing a partial taking down of the apparatus is the refilling with sulphide.

University of Bristol, April 30, 1914.

Potassium Trioxide and the Stability of Alkaline Peroxides.—R. de Forcrand.—The heat of formation, starting from the elements, of the four alkaline trioxides, Na_2O_3 , K_2O_3 , Rb_2O_3 , Cs_2O_3 , is practically the same, viz., +126 cal. The passage from the monoxide to the dioxide disengages quantities of heat which regularly increase from calcium to caesium:—Ca, 4.11; Li, 7.97; Sr, 13.07; Ba, 18.36; Ra, 18.7; Na, 19.03; K, 22.0; Rb, 24.1; Cs, 25.0.—*Comptes Rendus*, clviii., No. 14

MOISTURE IN CLOTH.

By WILLIAM M. DOHERTY, F.I.C., F.C.S.

IN volume cviii. (August 22, 1913) of the *CHEMICAL NEWS* there appeared a short article by Mr. E. G. Bryant, B.A., B.Sc., of Port Elizabeth, South Africa, in which is noted the amounts of hygroscopic moisture found in woollen cloth at the above named locality, the said amounts being 12 per cent and 14 per cent respectively. A request for comparison with moisture content of a similar fabric in other parts of the world is expressed, the idea being to see if there are noted differences in "condition" produced by different geographical positions. The subject is perhaps an important one, and I give here my experiences in Sydney, New South Wales. Occasionally during a long period of years I have had to determine the moisture in ordinary woollen cloth, and the results always approximated 10 per cent, which I had considered the normal figure for this part of the world. But as the purpose for which my tests were made was to enable me to calculate analyses results on dry material simply, no notice was ever taken of humidity or temperature of air at the time of making the determinations. Since reading Mr. Bryant's article I have determined the hygroscopic moisture in various kinds of woollen fabrics, noting at the same time the relative humidity and also the temperature of the atmosphere. The method used in expelling the moisture was to heat in a water-oven (98°C.) until constant. The results were as follow:—

Kind of fabric.	Relative humidity. Per cent.	Shade Temp. $^{\circ}\text{F.}$	Moisture. Per cent.
1. Diagonal serge	57	77	9.81
2. Closely woven worsted	57	77	9.96
3. Coarsely woven tweed	57	77	9.85
4. Berlin wool	60	74	10.00
5. Blanket	63	75	10.91
6. Closely woven tweed ..	89	76	10.93
7. Blanket	85	75	11.50

The degree of humidity seems here to exercise an influence on the moisture content, allowing for the apparent higher hygroscopic quality of the blanket. The amounts in Nos. 6 and 7 were the highest I had yet found, and I re-weighed the pieces after exposure to the air for some days, when the moisture was practically restored. But to obtain this latter result, final weighings had to be made following upon humidity and temperature being identical with those at initial weighings. A further test was made with a piece of high-class blue-back diagonal serge, which consisted of weighing the piece daily, simultaneously noting humidity and temperature. The results were:—

Relative humidity. Per cent	Temperature. $^{\circ}\text{F.}$	Weight of piece. Grms.
76	77	9.187
89	76	9.214
61	75	9.204
58	74	9.182
49	74	9.176
52	76	9.158
69	77	9.180

Here it will be seen that the greatest humidity does synchronise with the greatest weight. The reverse tendency is also in the appropriate direction, though the figures do not quite coincide. But this lack of absolute coincidence is I think due to lag, which most probably is a disturbing element in such an experiment as I am here describing. I have noticed that some days may elapse (humidity and temperature being equal) before the last amounts of moisture be restored to the dried cloth on

simple exposure. The above weighings were made of course under shade conditions wholly, and I found that if the same piece of cloth was exposed to the direct rays of the sun for three hours the weight had fallen to 8.64 grms., that is to say the greater part of the moisture had been expelled.

A final experiment was made during the prevalence of very wet weather, the piece being weighed on a wet day after the rain had been falling more or less continuously for three days. The relative humidity at time of weighing was 90 per cent, and the temperature 77°F. The greatest previous weight was 9.214 grms., and it had now risen to 9.453 grms, an increase of 2.5 per cent. The total percentage of moisture in the cloth on this last occasion was 13.7, thus, during rainy weather, practically reaching the amount found by Mr. Bryant at Port Elizabeth.

Ordinarily, then, the amount of hygroscopic moisture in cloth in Sydney is less than that found by Mr. Bryant in Port Elizabeth. Probably meteorologically the two ports are about on a par as far as this question is concerned.

It should be noted perhaps that these experiments were made in February and March.

Government Laboratory,
Department of Public Health,
Sydney, N.S.W.

FLUIDS WITH VISIBLE MOLECULES.

IN a course of four lectures given recently at King's College, London, Prof. Jean Perrin, of the University of Paris, gave an interesting account of his work on the experimental verification of the molecular hypothesis.

The kinetic theory of gases gives an approximate means of determining the actual dimensions of the molecule, and Maxwell obtained an expression for Avogadro's constant N , from considerations connected with the viscosity of gases. The Brownian movement of visible microscopic particles appears to be the result of molecular agitation, and any particle in suspension seems to function as an enormous molecule. If this is so, the gas laws, already extended by van't Hoff to solutions, must also apply to dilute emulsions composed of equal grains, and if the osmotic pressure of this "gas with visible molecules" is known Avogadro's Law will give the ratio of the masses of the grains to those of the invisible molecule of any gas. In an indefinite vertical column of emulsion in equilibrium the osmotic pressure at any level counterbalances the weight of the higher layers, as in a heavy gas, and the emulsion is a miniature atmosphere. If, then, it is necessary to rise a hundred million times less than in oxygen in order to double the rarefaction, it may be concluded that the visible grain is a hundred million times heavier than the molecule of oxygen. In order to obtain equal grains emulsions made by precipitating alcoholic solutions of resin with water were submitted to a process of fractional centrifugation. These emulsions obey the gas laws, and the value of Avogadro's constant N can be calculated from them. It is found that the value of N thus found is independent of the size of the particles, and agrees with the number given approximately by the kinetic theory (68×10^{22}). The Law of Gay Lussac holds good for temperatures between -10° and $+60^{\circ}$. Since dilute emulsions follow the gas laws it is probable that concentrated emulsions would behave like compressed fluids, and that van der Waals' theory could be applied in studying them. To determine the osmotic compressibility of the emulsion (*i.e.*, the variation of the osmotic pressure as a function of the concentration of the grains) it is necessary to observe the distribution in a vertical column of emulsion, all the grains of which have been counted. The osmotic pressure at each level, supporting all the grains above this level, is thus determined. (The emulsion is its own manometer).

It is then easy to determine whether the pressure P thus obtained satisfies van der Waals' equation—

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

where R = gas constant.

T = absolute temperature.

V = volume of emulsion containing N grains.

b = four times the volume of these grains.

a = a constant corresponding to the cohesion.

If this is the case the observation of a concentrated emulsion will give Avogadro's number. Experiment verifies this prediction; it is found, however, that the constant of cohesion is negative, and that the grains repel one another to an appreciable distance. This result permits of the experimental determination of the thickness of the double layer of electrification by contact, and throws light upon the properties of colloidal solutions. A knowledge of the compressibility also provides a verification of the theory of Smoluchowski on the spontaneous fluctuations of the density of a fluid in a given volume. The activity of the Brownian movement is defined as the quotient $\frac{E^2}{t}$, where

E^2 is the mean square of the displacement in time t . An emulsion should diffuse like a solution of visible molecules with a speed which is greater the greater the speed of the molecules composing it. By calculation it is found that the coefficient D of diffusion is obtained by dividing the activity $\frac{E^2}{t}$ by 6, and since at any level as many molecules pass upward by diffusion as pass downward by gravitation the coefficient of diffusion depends upon the radius r of the grains and the viscosity η . Thus Einstein's equation holds, viz.:—

$$\frac{E^2}{t} = 6D = \frac{RT}{N} \frac{1}{\pi r \eta}$$

Thus Avogadro's constant can be determined both by measuring the diffusion and by measuring the displacements. In order to study the diffusion emulsions were obtained which were such that the grains remained attached to the walls of the vessel when they came in contact with them. The emulsion thus became progressively weaker by diffusion, and the coefficient of diffusion was given by the increase of the number of grains captured as a function of the time. The displacements of spherules of known radius can be measured very easily, and these measurements, made in very varying conditions as regards the size of the grains and the nature of the intergranular liquid, all gave concordant results for Avogadro's number. Moreover, with relatively large spherules it is easy to measure the rotations, and thus verify Einstein's formula for the Brownian movement of rotation. All these theories apply to granules suspended in a gas, except that Stokes's law no longer holds good. By applying an electric field Townsend's equation for the diffusion of gaseous ions connects the charge e on the granule with Avogadro's number and with the activity of its Brownian movement, viz.:—

$$Ne = \frac{RT}{D} \frac{u}{H} = 6RT \frac{t}{E^2} \frac{u}{H}$$

The verification of these formulæ giving for the product Ne simple multiples of the faraday shows that the charge of microscopic particles is an integral multiple of the same charge (equal to that of the hydrogen ion in electrolysis).

The following table shows the results obtained by the different methods briefly described above:—

	Quotient $N/10^{22}$
Viscosity of gases	62
Brownian movement of translation	69
Brownian movement of rotation	65
Fluctuation	60
Electric charge of droplets	65
Radio-activity	62
	65

CHEMICAL REACTIONS AT VERY LOW PRESSURES.*

I.—THE CLEAN-UP OF OXYGEN IN A TUNGSTEN LAMP.

By IRVING LANGMUIR.

(Continued from p. 246).

Electron Theory of Chemical Combination.

WE have seen that the impact between oxygen molecules and tungsten atoms cannot be the determining factor in the reaction of oxygen with hot tungsten. The fact that the velocity of the reaction is not affected by the temperature of the oxygen indicates that the oxygen molecules react primarily with particles of very much smaller mass than themselves, therefore presumably with free negative electrons in the metal.

Since the mass of the electrons is very small, their velocity must be very large in order that they may have the same average kinetic energy as the atoms of tungsten.

From Equation (16) we see that when two particles collide the amounts of impact contributed by each are proportional to $\sqrt{1/M}$. If we consider the impact between oxygen molecules with an average temperature of 298° and negative electrons with velocities corresponding to 1600° , we find that the share of the impact contributed by the oxygen is to that contributed by the tungsten as $\sqrt{298/32}$ is to $\sqrt{1600/0.00055}$. That is, the movement of the oxygen molecule is only $1/560$ as effective as that of the electron. This difference is so great that we can neglect the velocity of the oxygen entirely in its effect on the reaction.

We have assumed that it is necessary for an electron and an oxygen molecule to collide with an impact exceeding a certain lower limit, in order that chemical combination may ultimately result. Since the velocity of the oxygen molecules is of so little importance, it is simply necessary, for chemical combination, that the electron shall strike the molecule with a velocity which exceeds a certain limit v_0 .

Let us now calculate what proportion of the electrons in a metal reach the surface with a velocity exceeding a certain value v_0 , and let us determine how this proportion increases as the temperature of the metal increases.

This calculation is identical with that made by Richardson in determining the number of electrons that escape from incandescent metals (*Phil. Trans.*, 1903, cci., 516).

Let N be the number of electrons in each cc. of the metal. Then, according to Maxwell's law, the number dN per cc. which have velocity components perpendicular to the surface of the filament lying between v and $v + dv$ is—

$$dN = \frac{N}{\sqrt{\pi}} e^{-(v/a)^2} dv/a \quad \dots (19)$$

where—

$$a = \sqrt{2/3} v \quad \dots (20)$$

Here $\bar{v}$ is the square root of the mean square velocity of the electrons in the metal, and can be calculated by Equation (4)—

$$\bar{v} = \sqrt{\frac{3RT}{M}} \quad \dots (21)$$

The number of electrons dn with velocities between v and $v + dv$ which reach a unit surface of the metal per second can be obtained by multiplying the number per cc. having this velocity by the velocity component perpendicular to the surface. That is, from (19)—

$$dn = v dN = \frac{N}{a\sqrt{\pi}} v e^{-(v/a)^2} dv \quad \dots (22)$$

* Paper read before the New York Section of the American Chemical Society. From the *Journal of the American Chemical Society*, xxxv. No. 2.

The total number of electrons which reach the surface with a velocity perpendicular to it exceeding a certain value v_0 is therefore—

$$n = \frac{N}{a\sqrt{\pi}} \int_0^{\infty} e^{-(v/a)^2} v dv = \frac{aN}{2\sqrt{\pi}} e^{-(v_0/a)^2}. \quad (23).$$

By combining this with (20) and (21) we obtain—

$$n = N \sqrt{\frac{RT}{2\pi M}} e^{-Mv_0^2/2RT} \quad (24).$$

The velocity v_0 is the velocity which the electron must have in order that it can combine with an oxygen molecule. As the temperature of the metal varies, the number of electrons having this necessary velocity will increase according to Equation (24). Therefore ϵ , which measures the rate of the reaction of oxygen with the tungsten, would be proportional to n . We may assume that N and v_0 do not vary with the temperature, and thus obtain from (24) a relation of the form—

$$\epsilon = B \sqrt{T} e^{-b/T} \quad (25),$$

where—

$$b = Mv_0^2/2R \quad (25a).$$

Taking the logarithm of (25), we get—

$$\ln \epsilon = -b/T + \ln B + \frac{1}{2} \ln T \quad (26).$$

Differentiating—

$$\frac{d \ln \epsilon}{dT} = \frac{b}{T^2} + \frac{1}{2T} \quad (27).$$

This equation differs from Arrhenius's Equation (11) only by the addition of the term $\frac{1}{2T}$. For all ordinary chemical reactions this term is very small compared to the first term.

The data for ϵ in Table IV. were compared with this equation. By taking $B = 0.85$ and $b = 12830$, Equation (26) gives the results in the fourth column of Table IV. These agree as well with the observed values of ϵ as do the results in Column 3 obtained from Arrhenius's equation.

We are thus able to derive a correct form of equation for the reaction velocity from Maxwell's distribution law.

Knowing now the numerical value of b , we can calculate the actual velocity v_0 of the electrons necessary to bring about a reaction. From—

$$v_0 = \sqrt{2bR/M} \quad (27a).$$

Substituting $b = 12830$, $R = 83.2 \times 10^6$, $M = 0.00055$, we find—

$$v_0 = 62.4 \times 10^6 \text{ cm. per sec.}$$

This velocity is small compared to that of cathode rays.

It is of interest to know through what voltage drop an electron would have to pass in order to attain this velocity. We have, if P = drop in potential,—

$$P = \frac{1}{2} (m/e) v_0^2.$$

For electrons $e/m = 18.0 \times 10^6$ e. m. units.

Whence the potential drop is 108.0×10^6 e. m. units or 1.08 volts. It is probably significant that this is the order of magnitude of the voltage necessary to decompose most chemical compounds.

Let us now calculate what proportion of all the electrons reaching the surface do so with a velocity exceeding v_0 . If we place $v_0 = 0$ in (24), we find that the total number of electrons reaching the surface is—

$$n_0 = N \sqrt{RT/2\pi M} \quad (28).$$

The proportion of these which have a velocity exceeding v_0 is therefore equal to $e^{-Mv_0^2/2RT}$, or, in other words, to $e^{-b/T}$. This ratio is given in Column 3, Table V.

The relative number n/n_0 of electrons striking the oxygen molecules which actually combine with them is very small. For example, if we consider a filament at 1270° being struck by 970 oxygen molecules, we see from

the value of ϵ that on the average only one of these will combine with the tungsten.

TABLE V.

I. Temp.	II. ϵ observed.	III. n/n_0 .	IV. $\epsilon n_0/n$.
1270° K	0.0011	0.000041	27
1470	0.0053	0.000162	33
1570	0.0094	0.000282	33
1770	0.0255	0.000715	36
2020	0.049	0.00173	28
2520	0.12	0.0062	19

On the other hand, we see from the value of n/n_0 that in order for one electron to combine with an oxygen molecule $1/0.000041$ or about 24,400 electrons must collide with oxygen molecules without combining. This leads us to the conclusion that each oxygen molecule striking the filament will, on the average, be struck by about 27 electrons. The number of electrons striking each oxygen molecule is equal to $\epsilon n_0/n$ in the fourth column. The average is about 30, and up to 1800° does not vary much with the temperature.

The number of electrons which strike each oxygen molecule depends on the number of electrons per unit volume in the metal, on their velocity, and on the forces the electron has to overcome in moving from the interior of the metal to the point where it collides with the oxygen molecule. If we assume that these forces are negligible, we may roughly calculate the number of electrons per unit volume.

Let us assume provisionally that the average distance between the electrons in the metal is about the diameter of an oxygen molecule. Since there are six possible directions perpendicular to each other in which an electron may move, we may consider that only one-sixth of all the molecules are moving towards the surface at any one time. If the velocity of the electrons and oxygen molecules were the same, then the chance that an electron would strike a molecule during a collision of the latter with the metal would be one-sixth. We can therefore readily see that the number of electrons which would strike the oxygen molecules during a single collision would be equal to $1/6 v_2/v_1$, where v_2 is the average velocity of the electrons and v_1 the average velocity of the oxygen molecules. The mass of an oxygen molecule is about 58,000 times as great as that of an electron. If the temperature of the oxygen and metal were the same, the velocity of the electrons would be $\sqrt{58,000}$ or 240 times that of the molecules. As the temperature of the oxygen is lower than that of the metal, this ratio would be somewhat larger—probably in the neighbourhood of 400. In this case $1/6 v_2/v_1$ becomes 67. This represents the number of electrons which would strike an oxygen molecule if the average distance between the electrons in the metal were equal to the diameter of the oxygen molecule. The atomic volume of tungsten is about one-third of the molecular volume of oxygen. If we should assume there is one free electron for each atom of metal, then we should expect 3×67 or 200 electrons to strike each oxygen molecule during a collision. The results of our experiments have already led us to conclude that the number of collisions is about 30. This would indicate that there are about one-seventh as many free electrons as there are tungsten atoms. It must be remembered, however, that this conclusion has been reached by assuming that no work is required to move an electron from the interior of the metal to the surface where it can collide with the oxygen molecule. If such forces do exist opposing this motion, then there must be more than one-seventh as many electrons as tungsten atoms. In any case, it is significant that we find the number of electrons so nearly equal to that of the tungsten atoms.

The question arises as to whether the impact from a smaller number than 30 electrons might not be sufficient to drive away an oxygen molecule. The momentum of a

molecule moving with a velocity corresponding to the temperature T is proportional to $\sqrt{MT}$. If we take the momentum of the electrons in the metal at 1600° as unity, we find for the momentums of—

Electrons in metal	1
Tungsten atoms in metal	570
Oxygen molecules at 300°	100
Oxygen molecules at 1600°	240

The average momentum taken up by the oxygen is $100 + 240$ or 340 . The collision of one electron against an oxygen molecule is only capable of giving it the momentum $2 \times 1 = 2$. It would require, therefore, the impact from 170 electrons to give the oxygen molecule the velocity it must have when it leaves the surface of the metal. This would indicate that about 8 per cent of its momentum is obtained by impact against tungsten atoms and only about 15 per cent from collisions with electrons.

We see, then, that our conclusion that each oxygen molecule is struck by 30 electrons, does not lead us into any inconsistencies, but leads to results which are in themselves probable.

(To be continued).

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

THE VULCANISATION OF RUBBER BY THE ULTRA-VIOLET RAYS.

Prof. Dastre, Member of the Academy of Sciences, in the names of Messrs. André Helbronner and Gustave Bernstein, has communicated a paper concerning the vulcanisation of rubber solutions by ultra-violet rays. The action of these rays on solutions of rubber to which sulphur has been added produces a combination between these two bodies without, however, the rubber, although vulcanised, being precipitated from the solutions. Contrary to what might be expected, remarkably stable solutions are thus obtained, and these solutions give, by evaporation, a perfectly insoluble pellicule. The analysis of the phenomenon enables one to follow, step by step, the process of vulcanisation. The ultra-violet rays do, indeed, precipitate the sulphur and depolymerise the rubber. These are two concomitant actions, combined with the repolymerisation of the rubber under the action of the sulphur, which constitute the vulcanisation of which the intimate nature is thus revealed, and completely confirms the theories already expressed by one of the authors. If we pass now to the practical side of the matter, the solutions vulcanised by the ultra-violet rays have an interesting future before them. They enable all kinds of repairs to be effected for any object in rubber. A veritable autogenous soldering is thus obtained of this matter, resisting heat or any other mechanical action, and it thus becomes unnecessary to perform an ulterior vulcanisation, which long and delicate operation was before obligatory. It is then quite a little revolution for all repairs, and especially that of rubber tyres. This interesting discovery will also have most important applications in the industry of rubber clothes, of envelopes of dirigible balloons, of shoes, &c.

MICROBIAN DROPLETS.

M. Roux has summed up the works of M. Trillat, of the Pasteur Institute, and M. Tanassier, concerning the formation of microbial droplets in the atmosphere and their properties. The authors have first shown that microbes can play the rôle of a nucleus for the condensation of humidity in the air, which explains the presence of numerous microbial drops, which are so much the lighter as the germ inclosed is smaller. The speed of the fall of these droplets follows the law of Stokes. MM. Trillat and Tanassier have studied the action of cooling on these

microbian droplets. Whereas the total cooling of a microbial mist, like that of a sudden decompression, has the effect of resolving the drops into rain and of purifying the atmosphere, the lowering of the temperature of one point of a microbial atmosphere determines an immediate transport of the germs that assemble and are localised in the cooled regions. The case is striking for the cooling surfaces. The knowledge of these results throws some light on the transmission of certain diseases by the intermediary of microbial droplets. Perhaps, in the future, some applications may be made for the purification and salubrity of rooms, halls, hospital wards, &c.

MUSICAL SENSATION.

Very curious experiments, especially interesting to musicians, have just been made by Dr. Marage. In a recent study he had shown that for each vowel there exists a note on which a minimum of energy is necessary to make it heard; that is, indeed, the origin of the telephonic "allo." Dr. Marage, in a paper presented before the Academy of Sciences by Prof. d'Arsonval, studies the sensibility of the ear for certain musical sounds. The question was to know the impressions experienced by an audience composed of musicians, savants, literary men, and society people, while listening to the same pieces of music of the sixteenth and seventeenth centuries, performed successively on the piano and on instruments of the period: clavessin, clavicord, lute, and viol. To realise this experiment the three hundred pupils who follow the classes at the Sorbonne of the physiology of speech and singing have been divided into two series. The pupils were to note their physiological and musical impressions. Out of an audience of 300 only 142 copies were given in; that is to say, that over 50 per cent of the pupils had no impressions or did not wish to write them down. And yet the copies were anonymous. The other half, however, on the contrary, experienced very diverse sensations. The pupils who gave in their copies were divided into 51 professional musicians or singers—25 cultivated persons, that is to say, with a good knowledge of music and studying it from a taste of the same, 34 with no musical knowledge, 13 scientific persons, professors, pupils of the Polytechnic School, of the Central School of Civil Engineers, or of the Sorbonne, and 19 literary professors or pupils. The copies, judged from the point of view of the analysis of the sensations, have given the following results:—The cultivated come out at the top of the list with 77 per cent of good copies; professors of singing and music come next with 62 per cent. The scientific pupils are greatly superior to the literary; 47 per cent of the first against 35 per cent of the second gave in excellent copies. The literary people make long descriptions, interesting and agreeable to read, but it is often difficult to discover what are the sensations they experience. The scientific, on the contrary, have clear ideas expressed in a few lines. Concerning the physiological impressions, it is to be remarked that almost all the audience is at first disagreeably impressed by the thin and metallic sounds of the clavessin, then the ear gradually gets used to these chords, new to it, and then it finds in them certain qualities. The grave sounds of the viols are immediately agreeable to the audience. M. Marage draws a practical and interesting consequence from these impressions; since grave sounds are agreeable to the ear and shrill sounds are disagreeable, motor-cars ought to have two sorts of trumpets; one with grave sounds for towns, not to be heard at a great distance, so as not to tire the citizens, and the other with a shrill sound that can be heard from afar, irritating the ear and forcing the peasants to pay attention. A curious phenomenon of suggestion has also been observed by M. Marage. After a first performance it was decided to change the piano. The instrument was new, and it had been thought that the sounds it gave forth were not very harmonious. Twenty musicians had expressed the desire to be present at the second series, at which the same programme was to be performed. They all noted down that

the new piano was very superior to the first one. Now, for some reason unknown to M. Marage, the instrument had not been changed, and was the same at both series. To sum up, Dr. Marage wonders if musical critics are not often influenced by the special dispositions of their auditive nerves. The particular action of vibrations on each nervous system, the habit of hearing certain sounds, and, lastly, the previous education, must deprive the artistic criticism of the value possessed by the scientific criticism. But, as Dr. Marage observes, these are important questions which can only be touched upon in passing.

A NEW SOUNDING APPARATUS.

The Prince of Monaco has presented before the Academy of Sciences a new sounding apparatus invented by M. Alphonse Berget, Professor at the Oceanographic Institute. This apparatus is based on the measure of pressure; it thus gives results that are independent of the curve that the sound line may take during its descent. It is based on the compression of a volume of water in a glass reservoir terminated by a slender tube, divided and coated with silver in the inside. An index of mercury, forming a piston, eats away the silvering as far as the point where it stops, so that when the instrument is drawn up it is possible to read the maximum pressure reached; that is to say, the depth. The indications of the apparatus graduated experimentally by the hydraulic press have only one correction, that of the temperature, which is made according to the table of Amagat; the depths that it measures are exact or only vary about 10 metres; that is to say, about an atmosphere.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 14, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Various Inclinations of the Electrical Axis of the Human Heart. Part I.A. The Normal Heart. Effects of Respiration." By Dr. A. D. WALLER, F.R.S.

"Fossil Plants Showing Structure from the Base of the Waverley Shale of Kentucky." By Dr. D. H. SCOTT, For. Sec. R.S., and Prof. E. C. JEFFREY.

"Controlling Influence of Carbon Dioxide in the Maturation, Dormancy, and Germination of Seeds." Part II. By F. KIDD.

The inhibitory effect of carbon dioxide on the germination of seeds previously described is dealt with in relation to temperature and oxygen supply. In relation to temperature the result obtained is unusual, the inhibitory action being more pronounced at low temperatures than at high. At 3° C. complete inhibition was obtained with 4 per cent CO₂; at 17° C. as much as 24 per cent had to be employed to obtain the same result. Varying partial pressures of oxygen also effect the inhibitory action of carbon dioxide, but to a less degree than temperature. Thus with 5 per cent oxygen, 15 per cent CO₂ produced inhibition; with 20 per cent oxygen, 27 per cent CO₂ was necessary. The author emphasises the fact that the adjustments of the moist seed by which it is enabled to continue dormant in the presence of oxygen and water, rather than those of the dry seed, are likely to have formed the central problem of seed life in nature. A low temperature and a decreased oxygen supply are often the natural conditions of a seed's environment in the soil.

Attention was called to the condition of restrained growth and to the non-sprouting of the embryos of many seeds while coming to maturity on the parent plant. The actual

CO₂ content of the tissues of such seeds is compared with that of similar seeds while actually sprouting. It seems probable that here also we may be dealing with an effect of carbon dioxide inhibition. Neither lack of water nor physiological insufficiency can account for the non-germination of the maturing embryos in the cases described.

In small amounts carbon dioxide is found to have a stimulatory effect on germinating seeds. The vitality of certain short-lived seeds is found to be prolonged under the influence of CO₂. Seeds of the rubber tree (*Hevea Brasiliensis*) treated in this way outlived those kept in commercial packing.

Correlating the results obtained in this and in a former paper, the author strongly emphasises the controlling influence of carbon dioxide in the biology of seeds. It appears that the normal resting stage of a seed is primarily a phase of narcosis.

"Cultivation of Human Tumour Tissue in vitro." By D. THOMSON, M.B., and J. G. THOMSON, M.B.

"Nutritive Conditions Determining the Growth of certain Freshwater and Soil Protista." By H. G. THORNTON and G. SMITH.

Experiments made on the growth of *Euglena viridis* in artificial media showed that, in addition to those inorganic constituents necessary for the growth of a green plant, which were supplied by Miguel's formula for growing Diatoms, a certain quantity of organic material, e.g., infusion of hay, was necessary. In order to determine the constituent in this organic material which stimulated growth, various pure substances, such as carbohydrates, tartaric acid, saccharin, allantoin, peptone, and various amido acids, were used in dilute solutions. Of these, only very weak solutions of amido acids favoured a really strong growth, the most favourable substances being tyrosin and phenyl-alanine which are very slightly soluble in water. In stronger solutions of alanine and glycocoll, bacterial growth interfered with the culture of *Euglena*. Tyrosin in the proportion of 1 in 24,000 gave an optimal growth, a fact which suggests that the amido acid acts as an auxiliary or stimulant rather than as the main source of nutrition.

Experiments with soil flagellates, especially *Trichomonas terricola* (Martin), showed that they could be cultivated in many solutions in which bacteria flourished, the flagellates feeding on several different kinds of bacteria.

Samples of various types of soil and water were tested for the presence of bacterial feeding flagellates, and these were found in all the samples, being most abundant in highly-manured soil. The wide distribution and abundance of these soil flagellates, and their very rapid growth in the presence of bacteria, suggests that they are of importance in the economy of the soil.

CHEMICAL SOCIETY.

Ordinary Meeting, May 7, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Alfred Archibald Boon, D.Sc., Heriot-Watt College, Edinburgh; John Vernell Cutler, Rose Cottage, Farringdon Lane, Ribbleson, Preston; Galstaun Shanazar Galstaun, B.A., Abbotsholme, Derbyshire; James Mylam Gittins, M.Sc., South Lynn, Limes Road, Folkestone; Alfred Holt, 32, Britain Street, Bury; John Cyril Jennings, Rosindell, Fairlop Road, Leytonstone, N.E.; Hashmat Rai, B.A., M.Sc., Chemical Buildings, Government College, Lahore, India; Frederic Robinson, M.Sc.Tech., The Hollies, Mile End, Stockport; Walter Edward Rowbottom, 23, Darville Road, Stoke Newington, N.; Alfred John White, B.Sc., Hawes Down, West Wickham, Kent. Messrs. W. Sloan Mills and P. C. Austin were elected

Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared as duly elected:—Abdel Hameed Ahmad, B.Sc.; Charles Frank Armstrong; Raymond Foss Bacon, B.Sc., M.A., Ph.D.; Arthur Baxter, B.Sc.; Frederick Stanley Baxter; Robert Reginald Baxter, B.A.; Charles Wesley Bayley; Robert Odell Bishop; Edward Godfrey Bryant, B.A., B.Sc.; Albert Coulthard, B.Sc., Ph.D.; Robert Barclay Craig; Robinson Percy Foulds, M.Sc.; Hugh Miller Galt, B.Sc., M.B., D.P.H.; Brojendranath Ghosh, M.Sc.; Clifford Girdlestone Gill; Alfred Cornwall Harrison; Richard Selwyn Haskew; Jaroslav Heyrovsky, B.Sc.; Arthur Bertram Hobson, M.Sc.; Trevor Edward Hodges; Lawson John Hudleston; Ralph Waldo Emerson MacIvor; Birendranath Maitra, M.Sc.; Yusuf Ismail Mulla; William Whalley Myddleton, M.Sc.; Arthur Ulysses Newton, B.Sc.; James Riddick Partington, B.Sc.; Walter Ryley Pratt, B.Sc.; Henry Ratcliffe; Walter William Reeve, B.Sc.; Herbert Corner Reynard, B.Sc.; John Rogers; Percy Charles Rundell; Lall Behary Seal; Max Herbert Tagg, B.Sc.; Norman Cecil White, B.A., B.Sc.; Albert Watkins Maggs Wintle.

Of the following papers those marked * were read:—

*115. "Researches on Santalin." Part II. By JOHN CANNELL CAIN, JOHN LIONEL SIMONSEN, and CLARENCE SMITH.

As a result of determinations of the molecular weight of certain derivatives of santalin by Barger's method, the authors are of the opinion that the formula previously assigned to this colouring matter should be doubled, and hence should be $C_{30}H_{28}O_{10}$.

The presence of four benzene rings in the santalin molecule appears also to be indicated by the facts that (1) the monomethyl ether yields, on oxidation, a mixture of anisic and veratric acids, and (2) nitrosantalin dimethyl ether yields four different benzenoid acids on oxidation.

Santalin yields anthracene on distillation with zinc dust (Grandmcugin), and the authors suggest that it is probably a dianthrane derivative.

DISCUSSION.

Dr. TURNER suggested that the low molecular-weight values found for santalin in phenol might be due to combination with the solvent. Of the other solvents employed, ether was most likely to lead to the simplest (or normal) molecular weight.

*116. "The Nature of Molecular Association. Its Relation to Chemical Combination." By WILLIAM ERNEST STEPHEN TURNER and SOLOMON ENGLISH.

The term "association" is frequently used to denote both the phenomenon of the formation of complexes of similar molecules and of dissimilar molecules (formation of molecular compounds). Further, views have been expressed to the effect that the formation of molecular compounds is a natural consequence of molecular association in the component substances.

In order to test how far these views are truly founded, the subject was investigated by a review of the different classes of substances which form molecular compounds and by an investigation of the behaviour in benzene, bromoform, chloroform, and water of mixtures of (1) alkyl and aryl haloids, (2) associated organic substances, (3) associated organic substances and alkyl or aryl haloids, (4) salts, (5) salts and alkyl or aryl haloids, (6) salts and associated organic substances, (7) alkyl or aryl haloids and iodine, (8) salts and iodine, (9) associated organic substances and iodine. A study was also made of the mixture of α -naphthylamine and phenol, in which combination is known to occur.

It was shown that whilst associated substances have a marked tendency to form molecular compounds, mixtures of associated substances can often be obtained without chemical combination, and, on the other hand, molecular compounds are also produced by non-associated substances.

Mixtures of salts in bromoform, so far from dissociating

each other, actually produce increased association. In one or two cases investigated the increased association passes through a maximum at a certain concentration, and then diminishes to zero. Similar behaviour is found in chloroform, and also in water, but in the latter to a less extent.

Benzoic and acetic acids have but little effect on one another, but in some other cases of organic associated substances, each constituent influences the other, probably by combination.

Alkyl or aryl haloids and iodine, and organic associated substances and iodine have but little effect on one another; a nitrate in bromoform solution acts with iodine to some extent, but not nearly so much as chlorides, bromides, and iodides, which form periodides, these in turn apparently becoming associated.

*117. "The Action of Diastase on Starch Granules." Part I. By JULIAN LEVETT BAKER and HENRY FRANCIS EVERARD HULTON.

Brown and Morris (*Trans.*, 1890, lvii., 510) have stated that when precipitated malt diastase is allowed to act at the ordinary temperature on the granules of barley starch, the whole of the optically active substance produced is maltose. Later Morris (*Trans.*, 1901, lxxix., 1085) confirmed the observation in the case of malt extract, but when precipitated diastase was used a smaller yield was obtained, and the product was stated to consist of a mixture of maltose and dextrin. No experimental evidence was adduced in support of this assertion.

The authors bring forward experimental evidence to show that the similarity to maltose of the specific rotatory power and the cupric reducing power of the products so formed at temperature varying between 15.5 and 37.5 is fortuitous.

On submitting the products of such action to fermentation, alcoholic fractionation, and dialysis, a dextrin was isolated which had a molecular weight exceeding 1500, an $[\alpha]_D$ of 177°, and a cupric reducing power varying between 11 and 20 per cent of maltose. This dextrin, which is not identical with the "stable dextrin" of Brown and Millar (*Trans.*, 1899, lxxv., 315), constitutes about 1/5th of the conversion products, from which crystalline maltose was also isolated, and a dextrin or dextrins of the same molecular weight and optical activity as maltose, but of much lower cupric reducing power. When the time of conversion exceeds three or four days dextrose is produced.

DISCUSSION.

Dr. PLIMMER pointed out that French observers consider that starch granules consist of two constituents.

The formation of small quantities of dextrose by the action of malt diastase might arise from one of these two constituents, and not from the other, which yields only maltose on hydrolysis.

In reply, Mr. BAKER said that he did not think that Maquenne and Roux's differentiation of the starch granule into amylocellulose and amylopectin affected the question of the formation of dextrose. If the dextrose were derived directly from one or other of these substances, it would be reasonable to expect its production at once, but the experimental evidence was against this. It was more probable that the dextrose was formed by the slow hydrolysis of some of the dextrins of low molecular weight present in the conversion products.

*118. "The Atomic Weight of Lead from Ceylon Thorite." By FREDERICK SODDY and HENRY HYMAN.

Recent results in radio-activity suggest that the lead derived from a mineral rich in thorium and poor in uranium may have an appreciably higher atomic weight than that of ordinary lead. If the end products of both uranium and thorium are, as is supposed, the isotopes of lead, the former should have an atomic weight of 206 and the latter of 208.4, whilst the accepted value for ordinary lead is 207.1. Ceylon thorite is uniquely suited for an experimental test of the question. The original analysis (W. R.

Dunstan, *Ceylon Mineralogical Survey Report*, March 31, 1904) gave 58.24 per cent of thorium, 0.38 per cent of uranium, and no lead. The authors' analysis gave 0.35 per cent of lead and 54.5 per cent of thorium. Whereas the chemical estimation of the uranium gave 0.72 per cent, a later preliminary estimation of the radium by the emanation method showed more uranium, namely, 1.6 per cent, and this is probably the more accurate. Owing to its greater rate of change, uranium will be about three times as effective in producing lead as thorium, so that if the lead in Ceylon thorite is entirely of radio-active origin, and if both isotopes are stable, the atomic weight should be 208.2.

Rather more than a grm. of the finally purified lead chloride was obtained from about a kilogram of the mineral, and used in the determinations. Exactly similar estimations with it and with ordinary lead chloride, purified by an identical series of processes, have shown that the thorite lead has distinctly the higher atomic weight. The determinations are purely relative, the atomic weight of ordinary lead being taken as 207.1. The method adopted followed, in part, that of Baxter and Wilson. The lead chloride was fused in hydrogen chloride before weighing, and its solution titrated with silver nitrate solution, the end-point being determined without an indicator by the cloud method. Two separate determinations showed a difference of between 0.4 and 0.5 per cent in the volumes of the silver nitrate solution required by equal weights of the two chlorides, whereas the errors of the estimation do not probably exceed 0.1 per cent. The relative atomic weight of the thorite lead calculated from the results is 208.4. The determinations so far carried out do not suffice to settle the question, but they show clearly a difference in the expected direction of the right order of magnitude.

From a preliminary examination with the Féry spectrograph, the spark spectra of the two specimens of lead, between 6656.3 and 2170, appear to be identical, except for the line 4760.1, which is much weaker in the thorite lead than in ordinary lead.

*119. "A Criticism of the Hypothesis that Neutral Salts Increase the Dissociation of Weak Acids and Bases." By JAMES WILLIAM MCBAIN and FREDERICK CHARLES COLEMAN.

It was shown that if the hypothesis of Acree, Bredig, Sneath, &c., is accepted, namely, that undissociated hydrochloric acid catalyses the inversion of sucrose better than hydrogen ion, and if, further, the data of A. A. Noyes and his collaborators are employed, not only do the data of Arrhenius (1899) for the acceleration caused by adding a neutral salt to a weak acid fail to prove that the dissociation-constant of the weak acid is enhanced by the presence of the neutral salt, but they may even be adduced as strong evidence against the existence of such an effect.

It was further pointed out that much of the evidence brought in support of the enhancement hypothesis is derived from methods often subject to grave systematic errors, involving, for instance, colour changes in colloidal or electrolytic colloidal systems, or distribution data—methods which are known in some cases to give highly distorted results. Here the results are conflicting in order of magnitude, and even in sign. The evidence of the electromotive-force measurements is also unfavourable to the hypothesis.

The authors conclude, therefore, that on the whole there is no experimental evidence for the supposed increase in the dissociation-constant of weak acids and bases caused by the presence of neutral salts.

120. "Studies in Substituted Quaternary Azonium Compounds containing an Asymmetric Nitrogen Atom. Part II. Resolution of Phenylbenzylmethylazonium Iodide into Optically Active Components." By BAWA KARTAR SINGH.

The author, in continuation of his work (*Trans.*, 1913, ciii., 604), has prepared externally compensated phenylbenzylmethylazonium iodide by two different methods, namely, (i.) by the action of methyl iodide on phenyl-

benzylhydrazine, and (ii.) by the action of benzyl iodide on phenylmethylhydrazine. In the second reaction there is also produced, owing to substitution having taken place, benzyldimethylazonium iodide, $(C_6H_5)_2(CH_3)_2(NH_2)NI$.

The resolution was effected with the aid of *d*-camphor- β -sulphonic and *d*- α -bromocamphor- β -sulphonic acids. In each case the first fractions consisted of pure *d*BdA component; in the last fractions the two component salts *d*BdA and *l*BdA formed solid solutions. The *l*BdA component could not therefore be obtained in a pure state, and the process of resolution was very slow and partial.

No mutarotation was observed in the case of any of the compounds obtained.

Several salts of the externally compensated and optically active azonium base were described.

121. "Contributions to the Chemistry of the Terpenes. Part XVII. The Action of Hypochlorous Acid on Camphene." By GEORGE GERALD HENDERSON, ISIDOR MORRIS HEILBRON, and MATTHEW HOWIE.

When treated with dilute aqueous hypochlorous acid camphene gives a quantitative yield of a chlorohydrin, $C_{10}H_{16}Cl \cdot OH$, a crystalline solid, m. p. 93°. This compound reacts readily with aqueous or alcoholic alkalis, yielding isocamphenylaldehyde, and by the action of phosphorus pentachloride is converted into camphene dichloride, $C_{10}H_{16}Cl_2$. *iso*Borneol is obtained by the action of zinc and alcohol on the chlorohydrin, which therefore is a chloroisoborneol. On oxidation with chromium trioxide the chlorohydrin is converted into a crystalline chloroketone, $C_9H_{15}Cl \cdot CO$, m. p. 132°, which gives camphor when heated with zinc and alcohol.

122. "Reactions by Trituration." By LESLIE HENRY PARKER.

It has been shown by Carey Lea (*Phil. Mag.*, 1892, [v], xxxiv., 46; 1893, xxxvi., 351; 1894, xxxvii., 31, 470) that shearing stress is capable of "disrupting the molecule" of many endothermic compounds, being far more efficient in this respect than simple pressure of enormous magnitude. This fact, combined with the results of Spring's work on the sulphates and carbonates of sodium and barium (*Bull. Soc. Chim.*, 1885, [iii.], xlv., 166; 1886, xlv., 299), was the cause of the present investigation into the interaction of various salt pairs, presumably in the solid state, by trituration.

Various pairs of salts were thoroughly dried, and ground together in a dry atmosphere. In most cases mutual action took place very easily, but not always. It was noticed that those substances which reacted most easily under the pestle were those which were easily fusible in ordinary circumstances, and *vice versa*, and the author arrives at the same conclusion as Johnston and Adams (*Am. Jour. Sci.*, 1913, [iv.], xxxv., 205), that shearing stress, or "non-uniform" pressure, causes local or surface fusion of the substance to which it is applied.

It can also be shown that the action of shearing stress is fundamentally different from that of simple pressure, the chief difference lying in the fact that the products of any reaction occasioned by shearing stress are not necessarily denser than the reacting substances. Experiments have also been conducted with the object of determining whether the trituration caused any ionisation of the atmosphere round the ground substances, but without success.

123. "The Reaction between Dilute Acid Solvents and Soil Phosphates." By JAMES ARTHUR PRESCOTT.

The author has investigated the action of dilute acid solvents on soil with respect to the amount of phosphoric oxide extracted. The extractions were made at constant temperature for varying lengths of time, and with initial concentrations of from 0.06 to 0.2 equivalents of acid per litre.

The amount of phosphoric oxide extracted is approximately proportional to the initial strength of the extracting acid. With nitric, hydrochloric, and sulphuric acids, an

increase in the time of extraction brings about a decrease in the amount of phosphoric oxide extracted. With citric acid the reverse is the case.

The amount of acid neutralised by the soil increases with the time of extraction, but an excess of acid always remains, large in proportion to the amount of phosphoric oxide present. The greatest diminution in the quantity of phosphate extracted with increase in time of extraction occurs with soils containing the highest proportion of clay. It is difficult to account for the removal of the phosphoric oxide from the solution on chemical grounds in view of the large excess of acid present, and the phenomena were therefore studied from the point of view of adsorption.

The results obtained by Hall and Amos (*Trans.*, 1905, lxxxix., 205) were found to agree with the adsorption relationship established by Freundlich, $Y/M = KC^{1/p}$, where Y = amount adsorbed by a quantity M of adsorbent, and C = equilibrium concentration of the solution.

For the Saxmundham soil $p = 0.58$; for the Broadbalk soils (5 and 8) $p = 1.63$; for the Hoos soil (2AA) $p = 1.14$.

In these results, a correction has to be made for the amount of phosphate still left in the soil.

The author has further investigated this point by adding known amounts of phosphate to a soil, and the curves obtained led to the conclusion that the amount of phosphate originally present in the soil, and soluble in hydrochloric acid, was the same as that soluble in citric acid.

For a soil from Agdell field, which had already been extracted twice with dilute acid, p was found to be 1.96 for hydrochloric acid, 0.06 equivalent per litre, and 0.485 for citric acid of the same acidity.

The same soil was also extracted seven times in succession with 2 per cent sodium hydroxide, and was found to contain no phosphate soluble in dilute acid solvents. Adsorption experiments could therefore be carried out without any correction whatever. The Freundlich law was found to hold, giving a value of $p = 2.22$ for hydrochloric acid and 2.08 for citric acid.

124. "Influence of the Dilution of Hydrogen Peroxide on the Velocity of Precipitation of Manganese from Ammoniacal Solutions in Presence of Zinc." By ANDREW JAMIESON WALKER and WALTER FARMER.

A study of the effect of dilution of the hydrogen peroxide on the accuracy of the results obtained in Jannasch's method for the separation of manganese and zinc in ammoniacal solution has shown that with a time-limit of thirty minutes precipitation of the manganese as $MnO(OH)_2$ is complete with solutions of hydrogen peroxide of 2.5 per cent strength. More concentrated solutions of the peroxide, up to 6 per cent, are equally efficacious. When the concentration is below 2.5 per cent, the manganese is not completely precipitated within the time indicated, the percentage error increasing in a marked degree with increase in the dilution. With such dilute solutions the manganese is precipitated as carbonate along with the zinc, so that under these conditions the percentage results obtained for zinc are too high. The influence of the dilution can be graphically represented by plotting curves with the percentages of hydrogen peroxide as abscissæ, and the percentage yields of manganomanganic oxide and of zinc carbonate as ordinates.

The table gives the results obtained in a series of nine experiments. 0.4142 gm. of $MnSO_4 \cdot 4H_2O$ should give 0.1417 gm. of Mn_2O_3 , and 0.4142 gm. of $ZnSO_4 \cdot 7H_2O$ should give 0.1806 gm. of $ZnCO_3$. This quantity of the salts was employed in each determination. The experimental error is much magnified by translation into percentage yield.

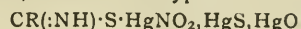
The zinc carbonate precipitated in the 6—2 per cent separations was quite white. As the dilution was increased, it developed a distinct light brown tint, due to the presence of manganese. Within the limits of experimental error, the deficiency in the percentage yields for manganese is balanced by the excess in the corresponding yields for zinc.

Percentage strength of H_2O_2 .	Mn_2O_3 Grm.	Percentage yield of Mn_2O_3 .	$ZnCO_3$ Grm.	Percentage yield of $ZnCO_3$.
6.0	0.1411	99.59	0.1815	100.53
5.0	0.1410	99.51	0.1815	100.53
4.0	0.1410	99.51	0.1815	100.53
3.0	0.1410	99.51	0.1816	100.59
2.0	0.1409	99.42	0.1817	100.61
1.0	0.1381	97.51	0.1861	103.99
0.75	0.1345	94.93	0.1915	105.99
0.5	0.1297	91.56	0.1995	110.49
0.3	0.1151	81.25	0.2206	122.19

The results indicate that in the separation of manganese and zinc in ammoniacal solution, hydrogen peroxide of not less than 2.5 per cent strength can be employed with satisfactory results (compare Jannasch and MacGregory, *Journ. Prakt. Chem.*, 1891, [ii.], xliii., 402; Jannasch and Niederhofheim, *Ber.*, 1891, xxiv., 3945; Jannasch and von Cloedt, *Zeitsch. Anorg. Chem.*, 1895, x., 405; Jannasch and Lehnert, *Ibid.*, 1896, xii., 134; Jannasch, "Gewichtsanalyse," Leipzig, 1897, 43).

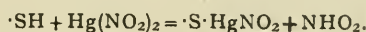
125. "Additive and Substitutive Compounds of Mercuric Nitrite with Organic Thio-derivatives." Part I. By PRAFULLA CHANDRA RAY.

Mercuric nitrite yields with methyl and ethyl mercaptans compounds of the type $(R \cdot S \cdot HgNO_2)_2, Hg(NO_2)_2, H_2O$, where R represents an alkyl group. With the substituted carbamides it forms compounds of the general formula— $NHR \cdot C(NH) \cdot S \cdot HgNO_2, 2HgS, HgO$; with thioacetamide and benzamide, nitrites of the type—



(R = alkyl or aryl); and with thioacetic acid a salt of the formula $CH_3 \cdot CO \cdot SH, Hg(NO_2)_2, HgS, HgO$. The compound with thioisocarbazine has the formula $2NH_2 \cdot NH \cdot C(NH) \cdot S \cdot HgNO_2, HgO, H_2O$, and that with dithiocarbamic acid $NH \cdot C(S \cdot HgNO_2)_2, HgS$.

With the thiocarbimides, also, compounds having the general formula $R \cdot N : CS \cdot Hg(NO_2)_2, 2HgS, HgO$ have been obtained; that with ethyl thioether has the formula $2Et_2S, 3Hg(NO_2)_2$. It is found that whenever a thio-compound tautomerises giving the thiol group, [for example, $CH_3 \cdot CS \cdot NH_2 \rightarrow CH_3 \cdot C(SH) \cdot NH$] the first reaction is as follows:—



126. "The Reactivity of Antimony Haloids with Various Types of Unsaturated Compounds." Part I. By ERNEST VANSTONE.

The eight binary systems formed by *s*-diphenylethane (dibenzyl), stilbene, azobenzene and benzil, and antimony trichloride and tribromide respectively have been investigated by thermal analysis.

s-Diphenylethane forms the compounds, $4SbCl_3, C_{14}H_{14}$, $2SbCl_3, C_{14}H_{14}$, and $4SbBr_3, C_{14}H_{14}$.

Stilbene forms the compounds $2SbCl_3, C_{14}H_{14}$ and $2SbBr_3, C_{14}H_{14}$.

The compounds with *s*-diphenylethane are stable; those with stilbene are unstable, and difficult to obtain. The tendency is to give a thermal diagram, showing a single eutectic point.

Azobenzene forms the compounds $4SbCl_3, C_{12}H_{10}N_2$ and $4SbBr_3, C_{12}H_{10}N_2$.

These compounds can only be obtained by seeding the fused mixture with some of the compound which had been prepared previously.

Benzil does not combine with antimony haloids.

The order of diminishing reactivity with antimony haloids is *s*-diphenylethane, azobenzene, stilbene, benzil.

It was shown that the magnitude of the optical exaltation increases in the same order.

The effect of increasing the number and position of phenyl groups and also of carbonyl groups on the reactivity with antimony haloids was discussed, and shown to be in agreement with the exaltation of molecular refractive power.

In all cases conjugation diminishes the reactivity with antimony haloids and increases the exaltation.

Thermal analysis thus provides a useful method of tracing the conjugation of the residual affinity of the unsaturated atoms and groups CH_2 , N , CO , with the phenyl groups in compounds of the type $\text{Ph} \cdot a \cdot a \cdot \text{Ph}$.

127. "The Absorption Spectra of Various Substances containing two, three, and four Benzene Nuclei." By JOHN EDWARD PURVIS.

The author has carried out an investigation of substances containing two, three, and four benzene nuclei united either with simple aliphatic residues or with inorganic radicals or elements, to see how far and in what directions the vibrations of the various centres influence the absorption phenomena, and particularly as regards the effect on the benzene bands. The substances examined were: *s*- and *as*-diphenylcarbamides, *s*-dibenzylcarbamide, *s*-diphenylthiocarbamide, triphenylguanidine, phenyl diphenylcarbamate, tribenzylamine, diphenyl phthalate, triphenylacetic acid, tribenzoin, triphenylphosphine, triphenyl phosphate, tri-*o*-tolyl phosphate, tri-*p*-tolyl phosphate, and tetraphenylsilicane.

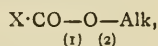
128. "Kinetics of the Decomposition of Acyl Derivatives of Phenols by means of Alcohol in Presence of Acids and Alkalis." (Preliminary Note). By MARIAN JONES and ARTHUR LAPWORTH.

The abstract of a paper by McCombie and Scarborough on "The Velocity of Saponification of the Acyl Derivatives of the Substituted Phenols" has recently appeared (vol. xxx., p. 107). The present authors have been engaged for more than a year on certain aspects of the subject, having taken up the work primarily with the object of throwing further light on the mechanism of the acid hydrolysis of esters.

Phenyl acetate has been most closely studied, special attention having been paid to the catalytic influence of acids and alkalis on the decomposition which it undergoes in alcoholic solution. With both agents the main reaction in the first instance consists in the irreversible formation of free phenol (or alkali phenoxide) and ethyl acetate, so that complete saponification is largely the result of two successive reactions, the second being saponification of ethyl acetate complicated by the formation of phenoxide.

The present authors have studied only the speed at which the first reaction takes place, by estimating the amount of phenol (or phenoxide) formed after varying periods. The influence of free phenol or phenoxide in excess has also been examined. Both acids and alkalis greatly accelerate the speed of the first reaction, and the relative influence of the two types of agent is of the same order of magnitude as in the case of the hydrolysis of alkyl esters, and there is therefore no reason to suppose that the mechanism of hydrolysis is different in phenyl and alkyl esters.

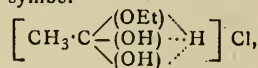
As phenyl is not detached from oxygen unless under conditions of exceptional severity, it must be concluded that hydrolysis of an ester, whether by acids or alkalis, involves the severance of the molecule at the point (1), and not at (2):



and the analogy to amides and allied compounds is complete.

It is now fairly generally agreed that during hydrolysis and esterification by acid catalysts a complex (ionised or non-ionised) of catalyst and the two principal reacting components is formed which may decompose so as to yield carboxylic acid and alcohol or ester and water (and catalyst) on the other. The symmetry of the reactions, combined with all the data now available, suggests that the hydrogen atom in the "polymolecule" is labile, in the intramolecular sense, and may be regarded as influenced

by all three oxygen atoms. The authors venture to suggest that the symbol—



which is not inconsistent with modern views on valency, is the most satisfactory one that can at present be devised for the hypothetical complex obtained during the hydrolysis of ethyl acetate by aqueous hydrochloric acid.

The work on the kinetics of the decomposition of phenyl acetate is being continued by one of the authors (M. J.), and examination is also being made of the applicability of phenyl acetate as an acetylating and dehydrating agent.

(To be continued).

FARADAY SOCIETY.

Ordinary Meeting, April 22, 1914.

Prof. ALFRED W. PORTER, F.R.S., in the Chair.

MR. CHARLES R. DARLING read a paper on "Recording Pyrometers," in connection with which a full display of the most recent types of instruments was exhibited.

After referring to the pioneer work of Le Chatelier and Roberts-Austen in connection with high temperature records, the author referred to the types of pyrometer at present in use, which were capable of yielding continuous records, and dealt with the special applications of each class. The requirements of modern furnace practice in relation to records were next dealt with, a distinction being made between instruments suitable for laboratory and workshop respectively. Typical thermoelectric recorders were then described, the essential features in all cases being (1) the intermittent contact of the pointer of the indicator with the moving chart, which, in conjunction with an inking device, produced a mark indicating the temperature; (2) an arrangement consisting of an automatic switch which enabled records from several pyrometers to be secured on the same paper. The special advantages of the Siemens-Halske, Leskole, Foster, Thread, Paul, and Leeds-Northrup recorders were described by reference to the actual apparatus. It was pointed out that any of these recorders could be used in conjunction with radiation pyrometers; the chart being specially divided for such purpose. Recorders for resistance pyrometers were next described, the advantage of this type being superior sensitiveness. The examples chosen for description were the forms due to Callendar, Paul, and Northrup. It was pointed out that as in the latest patterns of recorders considerable power is available, controlled by the pyrometer, it was highly probable that the automatic control of furnace temperatures would be realised in the near future, the mechanism being utilised to regulate the supply of gas, oil, electric current, or coal-dust when continuously fed. In conclusion, a tribute was paid to the National Physical Laboratory for the excellent work performed in standardising recorders and pyrometers generally, so that all types could now be relied upon to agree in their indications.

Dr. J. A. HARKER referred to the usefulness of the paper in view of the scarcity of literature on the subject, and he praised the excellence of the instruments exhibited. He hoped some information would be forthcoming with regard to the comparative life and efficacy of the various types. Some confusion in pyrometric measurements had sometimes arisen on account of the two systems of standardisation in use, namely, the usual method of comparison by reference to the melting-points of certain metals, and by reference to one fixed point, namely, the melting-point of potassium sulphate. This was often assumed, following the older workers, to be 1015°C ., whereas it was actually about 1070° .

Mr. R. S. WHIPPLE thought the difficulty of working the Callendar instrument had been overrated; over 400 of these were in use in charge of men not specially skilled.

Much work had been done with recorders in the control of heat supply. He instanced a steel works in which by the regulation of the hot-air mains a constant temperature of 700° C. was maintained to within 10°. A spectroscopic used for measuring the velocities of stars in the line of sight was being kept at a temperature constant within 100° C. He further instanced a large soldering iron used for tinsplate, where constancy of temperature was most important, which was being regulated by recorder control.

Mr. C. E. FOSTER dwelt on the necessity of educating the user to want control. He emphasised the advantages of base metal thermo-couples which gave large and constant e.m.f.'s.

Mr. E. H. RAYNER hoped the author would add to his paper a table of standard melting-points so that users of pyrometers could know what temperatures for standardising were recommended.

Mr. R. W. PAUL, referring to the motor drive, for which he disclaimed originality, said that it was necessary to have ample power so as to have a large margin to waste in governing. Surprising accuracy of speed was then attainable.

Mr. DARLING replied to the discussion. The Callendar instrument was admirable where there was no vibration. He agreed as to the future of base metal couples, as homogeneous alloys could now be obtained, but above 1200° C. radiation pyrometers should be used.

Dr. E. B. R. PRIDEAUX read a paper on "*Diffusion and Membrane Potentials*." (Will be inserted in full).

A paper by Dr. R. E. SLADE and Mr. W. G. POLACK on "*The Acidic and Colloidal Properties of Aluminium Hydroxide*" was read by Dr. Slade.

1. The conclusions of Mahin, Ingraham, and Stewart that aluminium hydroxide has no acidic properties are criticised.

2. Experiments on the conductivity of sodium aluminate solutions show that there is no evidence of the existence of colloidal aluminium hydroxide in these solutions, as was supposed by Hantzsch. Whenever hydrolysis takes place crystalline aluminium hydroxide is deposited.

3. An examination of sodium aluminate solutions in the ultra-microscope gave no definite evidence as to the existence or non-existence of colloidal particles. In the colloidal aluminium hydroxide solutions of Crum it was found that the number of microns present was very much greater than the number of submicrons.

Mr. A. M. WILLIAMS presented a "*Note on Negative Adsorption*."

The paper summarised the results of experiments in which it had been found that with some electrolytes in water the "adsorption" was at first positive, increased to a maximum, decreased, passed through zero, and then became negative. Attention was therefore drawn to the fact that with different concentrations of the same solution both positive and negative "adsorption" of the solute might be observed. Hence both solvent and solute must be regarded as being adsorbed.

Mr. J. H. ANDREW communicated a paper on "*The Embrittling of Iron by Caustic Soda*."

Small flat specimens of wrought iron, rough filed and highly polished, were immersed in a concentrated aqueous solution of caustic soda at 100° C. for periods lasting over several months. The specimens were examined from time to time, and it was found that—(1) The initial corrosion of the polished metal is less than that of the unpolished, but eventually both become highly crystalline, the surface of the two being similar, and their corrosion rate is approximately the same.

The re-crystallisation of the specimens causes them to become extremely brittle; the brittleness eventually disappears, however, with prolonged immersion, and during the treatment with soda, hydrogen gas is evolved.

The rate of corrosion of wrought iron increases with time, attains a maximum and then decreases, the corrosion, after a very prolonged immersion in caustic soda,

being extremely slight. It has been suggested that the corrosion is due to the iron being constituted of two phases, a crystalline phase and an amorphous phase, which surrounds the crystals and binds them together.

It is suggested that when a duplex metal of this nature is immersed in an aqueous solution of caustic soda, electrolysis sets in, iron going into solution at the anode, and hydrogen is liberated at the cathode, whilst sodium ferrite is formed in solution.

The hydrogen after giving up its charge at the cathode, is partially liberated and partially occluded by the metal. It is this occlusion of, and diffusion into, the interior of this hydrogen which brings about crystalline growth and brittleness in the metal, the hydrogen being first absorbed by the amorphous film existing between the crystals, thereby forcing the crystals apart. When both the amorphous and the crystalline metal have become saturated, or partially saturated, with hydrogen, the metal may be considered as constituting a hydrogen cell, the potential difference depending upon the concentration of the hydrogen in the two phases; this will be less than the potential difference between the two metallic phases, and the corrosion will diminish.

The decrease in brittleness after prolonged immersion is probably due to an equilibrium between the hydrogenised phases being established, the initial brittleness being due rather to the molecular rearrangement of the metal brought about by occlusion and evolution of hydrogen, rather than to the mere presence of hydrogen in solution. It is quite possible that the original amorphous material is destroyed, new amorphous material eventually being formed.

Experiments were carried out with the idea of showing that hydrogen actually did diminish the rate of corrosion. An electrolytic iron was heated to 1000° C. in hydrogen, and allowed to cool in the gas. The specimen after this treatment corroded extremely slowly, whereas another sample of the same material untreated corroded at the normal rate.

It may be concluded from these experiments that the passivity of iron produced by immersion in caustic soda is due to the decrease in potential difference between the crystalline and amorphous phases, produced by occlusion of hydrogen.

A 0.5 per cent carbon steel is affected to a much less degree by caustic soda solution.

The re-crystallisation of electro-deposited iron found by Stead and Carpenter to occur when the metal is allowed to slowly cool through the A_3 critical point, is explained upon the basis of hydrogen evolution; as the iron cools through the critical point the evolution of hydrogen effects a re-crystallisation of the metal.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 14, April 6, 1914.

Use of Manganous Oxide for the Catalysis of Acids. Preparation of Pentamethylene Aldehydes and Acetones. Formation of Cyclopentylamines.—Paul Sabatier and A. Mailhe.—Manganous oxide, obtained from manganous carbonate, can be used as catalyst in the formic reduction of acids at a temperature between 300° and 360°. The acid to be reduced is introduced into the catalysis tube with double the volume of formic acid. The portions of this latter acid, which are not used in the reduction, are totally converted into gaseous products. In the condensed product the water formed is eliminated and the aldehyde is separated from unchanged acid by fractionation. Cyclopentanone, C_5H_8O , can be obtained by the decomposition over manganous oxide at 350° of adipic acid. β -Methylcyclopentanone can be prepared similarly, and both substances readily yield oximes, from which cyclopentylamines and β -methylcyclopentylamines can be obtained by direct hydrogenation over nickel.

Nitride of Iron.—G. Charpy and S. Bonnerot.—When metallurgical ferrous products are exposed to the action of ammonia iron nitride of formula Fe_2N is formed. If very fine shavings of the metal are used it is quite easy to transform them completely into nitride. The nitride is reduced to ammonia by means of hydrogen at 350° . The velocity of the reaction increases rapidly as the temperature is raised and becomes very great at 500° to 600° . When the nitride is heated in nitrogen at atmospheric pressure decomposition does not begin till a temperature of 550° is reached. It is probable that the small quantities of nitrogen which are found in cast-irons and steels are present in the occluded state, or in a state of combination with an element other than iron.

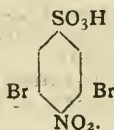
Atomic Weight of Nebulium and Temperature of Nebula of Orion.—H. Bourget, Ch. Fabry, and H. Buisson.—The very marked double line 3726–3729 in the ultra-violet is not attributable to any known gas. By the calculation of the limiting order of interference, which is a function of the atomic weight and the absolute temperature, it is found that the atomic weight of the unknown gas, nebulium, is about 3. The maximum temperature of the luminous gas is about 15000° . A strong green ray ($\lambda = 5006$) is also due to an unknown gas. It is emitted by a gas of atomic weight greater than that of hydrogen but less than that of the gas which emits the ultra-violet ray. It is noteworthy that, according to Rydberg's recent classification of the elements, there are two unknown elements between hydrogen and helium having atomic weights 2 and 3 respectively.

Quantitative Study of the Absorption of Ultra-violet Rays by Diketones of the Fatty Series.—Jean Bielecki and Victor Henri.—The absorption of acetone increases a little in alkaline and diminishes in acid solution. The presence of two carbonyls in the conjugate position produces an absorption band which is displaced 150–200 U.A. towards the red with reference to the characteristic band of a single carbonyl. Thus there is a hypsochromic effect. The presence of two separated carbonyls in the γ -position produces an augmentation of the characteristic band but no displacement; there is thus only a hyperchromic effect. The β -diketones show a spectrum which varies greatly according to the reaction of the medium and the nature of the solvent.

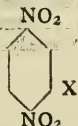
Atti della Reale Accademia dei Lincei.

Vol. xxiii. [i.], No. 5, 1914.

Nitrosubstituted Benzenes obtained from Corresponding Amino Derivatives.—G. Körner.—With many substituted anilines the substitution of an amide group by a nitro group is easily performed, and the yield is good. In other cases the reaction does not take place, or else the amount of substituted product obtained is negligible. An aqueous solution of dibromosulphanilic acid when treated with nitrous acid and an excess of sodium nitrite in aqueous solution gives the dibromonitrosulphonic acid—



In the same way the dinitrobenzene monohalogen derivatives of the type—



can be obtained, starting from the corresponding nitro-aniline. The author has prepared the 1.4.5-dinitrochloro, bromo, and iodo benzenes, and investigated their properties.

Researches in Systematic Chemistry: Ruthenium, Rhodium, Palladium.—G. A. Barbieri.—Trivalent ruthenium gives with acetyl acetone a crystalline red compound, monomolecular in bromoform, and soluble in the solid state in aluminium acetyl acetate. With molybdic acid rhodium forms complex compounds, rhodimolybdates, which both chemically and crystallographically are completely analogous to the corresponding complex molybdates of aluminium, Fe^{III} , Cr^{III} , and Co^{III} . Divalent palladium gives an acetyl acetate which is monomolecular in bromoform, and which forms mixed crystals with cupric acetyl acetate.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, June 2, at 3 o'clock, Prof. A. Fowler will begin a course of two lectures at the Royal Institution on "Celestial Spectroscopy"; on Thursday, June 4, Prof. Silvanus P. Thompson will deliver the first of two lectures on "Faraday and the Foundations of Electrical Engineering"; and on Saturday, June 6, Mr. S. Goetze will commence a course of two lectures on "Studies on Expression in Art." The Friday Evening Discourse on June 5 will be delivered by Prof. W. H. Bragg on "X Rays and Crystalline Structure," and on June 12 by His Excellency the Hon. Walter Hines Page (the American Ambassador) on "Some Aspects of the American Democracy."

Australasian Medical Directory.—Messrs. Butterworth and Co. (Australia), Ltd., 4, Bell Yard, Temple Bar, London, have just published "The Medical Directory (incorporating 'Loxton's Medical Directory') of Australia, Tasmania, New Zealand, Pacific Islands, Malay States, China, Japan, Hong Kong, &c.," by F. W. Loxton. Amongst the contents may be mentioned—Appointments in Hospitals, List of Doctors in Australasia, Commonwealth Census, Climates of Australasia, Particulars of Hospitals, Medical Boards in New South Wales, Queensland, Victoria, South Australia, and Western Australia, Registration in the Various States, New Zealand Medical Acts, List of Public Hospitals, &c. The volume also contains a section dealing with the Laws Relating to Medical Practitioners in the various states; Mr. Baxter-Bruce, of the New South Wales Bar, is responsible for this section.

MEETINGS FOR THE WEEK.

TUESDAY, 2nd.—Royal Institution, 3. "Celestial Spectroscopy," by Prof. A. Fowler, F.R.S.

WEDNESDAY, 3rd.—Society of Public Analysts, 8. "The Insoluble Bromide Value of Oils and its Determination," by Alexander Gemmell. "Determination of Iridium in Platinum-Iridium Alloys," by C. O. Bannister. "Symbolical Representation of Analytical Operations" and "Properties of some Chlorohydrocarbons and their Uses in Chemical Analysis," by L. Gowing-Scopes. "Changes in the Character of Fats during the Process of Cooking," by Helen Masters and H. L. Smith. "Chief Source of the Loss of Sulphuric Anhydride and of Chlorine by Ashing Substances containing these Constituents," by J. O'Sullivan.

THURSDAY, 4th.—Royal Institution, 3. "Faraday and the Foundations of Electrical Engineering," by Prof. Silvanus P. Thompson, F.R.S.

Chemical, 8.30. "Studies in the Succinic Acid Series—Part I, The Chlorides of Succinic and Methylsuccinic Acids and their Constitution," by G. F. Morrell. "Dilution Limits of Inflammability of Gaseous Mixtures—Part I, Determination of Dilution Limits; Part II, The Lower Limits in Air of Hydrogen, Methane, and Carbon Monoxide," by H. F. Coward and F. Brinsley. "Comparative Study of the Absorption Spectra of some Compounds of Phosphorus, Arsenic, Antimony, and Bismuth," by C. R. Crymble. "Reactions of β -Hydroxy- α -amino-compounds as Cyclic Structures," by J. C. Irvine and A. W. Fyfe.

FRIDAY, 5th.—Royal Institution, 9. "X-rays and Crystalline Structure," by Prof. W. H. Bragg, F.R.S.

SATURDAY, 6th.—Royal Institution, 3. "Studies on Expression in Art," by Sigismund Goetze.

THE CHEMICAL NEWS

VOL. CIX., No. 2845.

THE PREPARATION OF EYE-PRESERVING GLASS FOR SPECTACLES.*

By Sir WILLIAM CROOKES, O.M., F.R.S.

SINCE March, 1909—in connection with the Glass Workers' Cataract Committee of the Royal Society—I have been experimenting on the effect of adding various metallic oxides to the constituents of glass in order to cut off the invisible rays at the ultra-violet and the infra-red ends of the spectrum. The work has been done chiefly in my own Laboratory. I have been aided by Mr. Harry Powell, of the Whitefriars Glass Works, who prepared several pots of coloured glass from my formulæ on a much larger scale than could be made outside a Glass works. From these glasses cylinders and sheets were made.

The main object of this research is to prepare a glass which will cut off those rays from highly heated molten glass which damage the eyes of workmen, without obscuring too much light or materially affecting the colours of objects seen through the glass when fashioned into spectacles, but the work necessitated an examination of the screening properties of glass plates for ultra-violet and luminous light, and therefore the research was enlarged so as to embrace the three forms of radiation.

Radiation from Molten Glass.

In order to ascertain what rays are given off from molten glass I spent some time at the Glass Bottle Works of Messrs. Nuttall and Co., St. Helens, and took many photographs of the spectra of the radiations.

Photo-spectrographic and other examinations were made of the radiation emitted from the molten glass under working conditions. Full details of the experiments and results are given in this paper.

At the time I visited Messrs. Nuttall's Works light green bottle-glass was being made; the mixture is composed of silica, sodium sulphate, and calcium carbonate or sulphate. The materials are melted in a large fire-brick tank, heated by a flaming mixture of gas and air playing on the surface. The gas is made some distance from the furnace in a "producer." Gas and air are conducted by separate channels to the upper part of the tank, where they mix and burn, the flame reverberating from the arched roof and heating the glass mixture to the requisite degree.

The area of the tank of molten glass is about 82 square yards, and it contains from 300 to 350 tons of the mixture. There are several such tanks in the works. The tank is divided by a fire-clay partition into two unequal parts. At the lower part is an opening through which the melted glass can flow. The larger portion of the tank, where the materials are melted together at a high heat, has a surface of about 63 square yards. This is called the "melting end"; when the mixture is well fused and homogeneous the molten glass flows through the opening into the "working end" of about 19 square yards, where the heat is less and the glass is in a viscous state. Fire-clay rings of 18 inches internal diameter and a foot deep float on the surface of the viscid glass; any scum on the surface of the tank is thereby kept from contaminating the surface of the glass inside the ring. One ring floats opposite each working opening, and the workmen withdraw the requisite quantity of glass for each operation from the inner surface of the ring.

The light from the melting end of the tank, viewed through a working opening, was brilliant white with a tinge of orange; it was with difficulty the unprotected eye could make out any details. Viewed through dark glasses the surface of the metal in the tank appeared as a seething mass in constant commotion. The surface in the working end was more easy to see. It was of a bright yellow incandescence, and comparatively quiet.

It is not certain what the temperatures are at each end of the tank. So far as one could judge the temperature at the melting end is about 1500° C., and at the working end decidedly less—say, 1200°.

About each opening, especially at the melting end, thin white vapours rose and settled on the surrounding cooler parts. A piece of paper held in this vapour instantly ignited. Examined with a hand spectroscope the yellow line of sodium was seen to be brilliant in this vapour, but the light from the molten glass showed a continuous spectrum in which the sodium line was visible. On one or two occasions a black line was seen in place of the yellow sodium line, showing a reversal. Some of the condensed vapour was collected from the cool sides of the working opening and chemically examined. It was found to consist principally of sodium and calcium sulphates, with a little sodium chloride.

Photo- and Thermo-graphic Experiments.

The spectrograph used for taking photographs of the radiation from the molten glass is the one I described in *Roy. Soc. Proc.*, vol. lxxv., p. 237, May, 1899. It has two quartz prisms, each made up of two halves, one half being right- and the other half left-handed, according to Cornu's plan for neutralising the effect of double refraction. The collimating and camera lenses and the double condensers are also of quartz cut in the same fashion. The slit jaws are made of two acute angled quartz wedges, edge to edge. The refracting prisms are of 60° angle, and each face is 35 mm. by 42 mm. The lenses are 52 mm. diameter and 350 mm. focus. The condensers are plano-cylindrical, one being double the focus of the other. In order to ascertain the exact position of any part of the spectrum I might obtain from the radiation from the molten glass, I took photographs on each plate of an alloy of equal molecular weights of zinc, cadmium, tin, and mercury. This alloy gives throughout the photographic region lines, the wavelengths of which are well known.

The instrument sloped downwards, so as to allow the radiation from the surface of the melted glass to enter the condensers, prisms, and slit along the axis. To prevent the great heat injuring the spectrograph Mr. Nuttall allowed the opening to be bricked up, leaving a hole a few inches square in the middle. This was covered with an iron plate with a 2-inch hole in it, and over this a quartz plate was fixed.

Panchromatic films were used. These are sensitive beyond λ 7800 in the ultra-red, and to the highest ultra-violet rays which will pass through quartz (about λ 2100). Flexible films had to be used in preference to glass, as they had to follow the curvature of the focal plane. Many preliminary experiments were made to ascertain the extent of spectrum to be recorded, its best position on the films, and the exposures needed. The slit of the instrument was generally placed about 4 feet from the molten surface, and it was found that from ten to fifteen minutes were required to produce a faint image on development. On each film, immediately before the radiation picture was taken, a photograph of the spark spectrum of the quadruple alloy was impressed on the film, in such a position that the two spectra would overlap to a very slight degree.

No. 1 photograph was taken at the working end of the tank, where the temperature was lower than at the other end. An exposure of twenty minutes was given, the width of slit being 0.025 mm.

No. 2 photograph was taken in the same conditions as No. 1, but with an exposure of forty-five minutes.

No. 3 photograph was taken at the melting end, where

* Read before the Royal Society, November 13, 1913. From the *Philosophical Transactions of the Royal Society*, Series A, vol. ccxiv., pp. 1-25.

the heat was fiercest. The width of the slit was reduced to 0.1 mm., and an exposure of half-an-hour was given.

No. 4 photograph, at the melting end, was exposed for one hour.

No. 5 photograph, at the melting end, was exposed for two hours.

No. 6 photograph, also at the melting end, was exposed for three hours.

It was not found practicable to give longer exposures.

Whilst these experiments were in progress, other experiments at another opening at the hottest end were tried to see if X-rays could be detected. Sensitive films were wrapped in black paper and then in lead foil in which designs had been cut. These were exposed for varying lengths of time, as near as it was safe to put them to the radiation from the molten glass, bearing in mind that the heat might affect the films. On development, no image of the stencil designs on any of the films could be detected. These results confirm those previously obtained by Dr. Burch—that X-rays are not emitted by the highly incandescent molten glass.

A careful examination of the six photographs shows a general progressive character, the extent of spectrum photographed extending into the ultra-violet as the length of exposure increases.

The extent of spectrum into the region of the ultra-violet is conveniently shown in the following tabular form* :—

No. 1 photograph, exposed twenty minutes, extends to λ 4520.

No. 2 photograph, exposed forty-five minutes, extends to λ 4320.

No. 3 photograph, exposed thirty minutes, extends to λ 3790.

No. 4 photograph, exposed sixty minutes, extends to λ 3640.

No. 5 photograph, exposed 120 minutes, extends to λ 3595.

No. 6 photograph, exposed 180 minutes, extends to λ 3345.

Taking the ordinary limit of visibility to lie between λ 3900 and λ 7600, it is seen that with an exposure of three hours to the highest heats the strength of impression does not extend much into the ultra-violet. The heat rays are very strong, and if injury to the eye is caused by exposure to radiation from the molten glass, a protective glass should be opaque to the infra-red rays.

These being present in the radiation from molten glass in far greater abundance than the ultra-violet rays, the inference is that it is to the heat rays rather than to the ultra-violet rays that glass workers' cataract is to be ascribed. It is, however, certain that exposure to excess of ultra-violet light also injuriously affects the eye.

That the ultra-violet rays act on the deeper-seated portions of the eye is shown by the intense fluorescence of the crystalline lens induced by these rays.

Besides the invisible rays at each end of the spectrum, the purely luminous rays, if present in abnormal intensity, are found to damage the eye. It therefore would be an advantage if in addition the obscuring glass for the spectacles were to be of a neutral or grey tint.

Synthetic Preparation of Glasses.

It soon became evident that my best, if not only, chance of solving the problem was to make different glasses in my own Laboratory, with the addition of known quantities of pure metallic oxides and earths as colouring or absorbing materials. Lapidary apparatus for cutting, grinding, and

polishing was also necessary so that the synthetically made glasses could be cut into plates—polished so as to be tested photographically in the spectrograph already described—and also tested for the percentage of heat rays they obstructed.

Many preliminary experiments were made on the preparation of a clear and colourless glass or flux to serve as a basis for the colouring with the various metallic oxides. Finally, two kinds of soda glass not containing lead were chosen, and Mr. H. Powell, of the Whitefriars Glass Works, who had assisted me in the preliminary trials by supplying me with many kinds of glass of different composition and fusibility, made a quantity of these fluxes and supplied them in a crushed condition.

In my earlier laboratory experiments the mixture of colouring matter and granulated flux was put into a small "gold pot" of Morgan's Crucible Co., and gradually heated over a "Meker" gas burner. It is advisable to have one at least of the colouring constituents in the form of nitrate so that its decomposition by heat shall mix and stir the constituents. The decomposition of the nitrate causes a little frothing; therefore it is necessary to add the mixture gradually to the crucible, to avoid frothing over. When all is added and the contents well fritted, the hot crucible is removed to an electric furnace and the temperature slowly raised until the glass is quite fluid. It is stirred at frequent intervals with a stout platinum rod. After an hour the stirring is discontinued, and the temperature kept up for an hour and a-half. The current is then cut off, the openings in the furnace plugged with asbestos to prevent draughts, and the whole allowed slowly to cool to anneal the glass. In some cases the composition of the glass was such that the melting-point had to be raised above $1400^{\circ}\text{C}.$, and as this temperature was beyond the safe limit with the platinum strip furnace, a blast-furnace fitted with a "Lennox" electric blower was used; with this arrangement larger quantities of glass could be raised with safety to a much higher temperature.

There are two conditions I have endeavoured to secure of the finished glass—each of great importance. One, the most essential, is the absence of all streaks, striae, and irregularities of density; the other, the absence of air bubbles. The first is obtained by repeated stirring and perfect admixture; the freedom from air-bubbles is secured by leaving the glass in perfect repose while the heat is at the highest point. On these and other points I have been much aided by reading an early paper by Faraday "On the Manufacture of Glass for Optical Purposes," the Bakerian Lecture read before the Royal Society in 1829 (*Phil. Trans. Roy. Soc.*, 1830, p. 1). On a small scale it is almost impossible to avoid slight striae owing to differences of density caused by the long continued heat volatilising some of the soda. Faraday was much harassed by this dilemma in the manufacture of his optical glass, and tried many experiments to ascertain the cause. To get rid of air-bubbles Faraday used spongy platinum in powder sprinkled over or added to the bulk of the melted glass. This was found to act pretty well, making the bubbles rise in the same manner as a piece of bread causes bubbles to rise when thrown into a glass of effervescing liquid. To get the full benefit from this device, however, the glass must be kept perfectly quiet and at the highest temperature for a longer time than in my case was always practicable.

When the crucible has cooled slowly for about twelve hours it is removed from the furnace, and the solid cone of glass removed by breaking the crucible by a few judicious blows with a light hammer. The lump of glass is now taken to the lapidary's table, and slit across the middle and a plate cut from it, which is ground and polished to a determined thickness, usually 2 millimetres.

Testing Synthetic Glasses for Opacity to Ultra-violet Light.

The plates are now tested for the opacity of the glass to the rays of the ultra-violet end of the spectrum. The

* In connection with this table the following scale for correlating colours with wave-lengths will be useful:—

Wave-lengths 7230 and below = Infra-red.			
λ	λ	λ	λ
From 7320 to 6470 = Red.		From 5920 to 4550 = Blue.	
" 6470 " 5850 = Orange.		" 4550 " 4240 = Indigo.	
" 5850 " 5750 = Yellow.		" 4240 " 3970 = Violet.	
" 5750 " 4920 = Green.		" 3970 and above = Ultra-violet	

spectrograph with complete quartz train, already referred to, was used. By superposing on the radiation from a Nernst lamp the light from a high-tension electric discharge between poles of pure metallic uranium it is possible to produce a practically continuous beam extending from λ 2000 to λ 8000, and the absorption of such a beam of radiation, produced by flat plates 2 mm. thick of all my experimental glasses, has been thereby recorded.

To ascertain the amount of heat obstructed by the plates of glass I first used a Melloni's thermo-pile as described in his papers,* but I soon found that modification was needed as the pile responds to the orange and red rays as well as to the infra-red.

Plates of dark smoky quartz 2 mm. thick were tested with the thermopile, and it was found that they transmitted nearly all the heat whilst cutting off 80 or 90 per cent of the light. Biotite (black mica) exerts a similar effect, and is more easily experimented with than smoky quartz. For many years I have used biotite for cutting off light and transmitting heat; I accordingly investigated the properties of many specimens of black and dark brown mica to find out which would be best for this special purpose.

Selection of Black Mica (Biotite) for Diathermancy.

Samples of dark brown and black mica vary considerably in their power of obstructing light and transmitting the infra red rays. By the kindness of friends connected with the mining and importation of mica I have been able to examine a large number of samples from different parts of the world.

Some very fine pieces of black biotite were sent by Messrs. Attwater and Sons, who tell me they were mined by them in the extreme north of Norway from a cleft in a mountain at about 2000 feet. This mica is extremely regular in the thickness of the flakes which can be split from it, and the colour of thin pieces is uniform. A piece 0.07 millimetre thick entirely cuts off the luminous rays, and even the sun's disc is only just seen through a flake 0.06 millimetre thick.

In addition to specimens from Norway, Messrs. Attwater and Sons sent me black biotite from German South-East Africa, and some fine pieces of "black amber" mica from Africa. The African mica is uniform in colour, and easily splits into flakes of great regularity. The German mica is difficult to split into uniformly regular flakes, and therefore varies considerably in colour.

Messrs. F. Wiggins and Sons allowed me to select some large sheets of dark brown and black biotite from their stock. The sheets when split are uniform in colour, and in thicknesses below about 0.30 mm. are sufficiently transparent to allow the eye to detect a Nernst glower. Mica differs, however, in transparency, one flake from a sheet being opaque at 0.24 mm., while a flake from another part of the same sheet is slightly transparent in a thickness of 0.34 mm. I also received good black mica from Mr. Henson, who gave as its locality Renfrew, Canada.

Many experiments have been carried on with all these kinds of brown mica to find a quality which would cut off the rays which at Kew were called the "scorching rays" (the infra-red rays), and some of the best results were obtained with the Norwegian mica from Messrs. Attwater and Sons, and the Black Amber African mica from Messrs. Wiggins and Sons.

There is a certain gradation of transmitted rays according to the thickness of the dark brown micas. All of them cut off rays at the blue end of the spectrum, and as the thickness increases the portion of the spectrum obstructed rapidly tends towards the red end, until a mica is found which affects the photographic plate in a narrowed

band round the line B, the exposure being from ten to twenty times as long as would be required for this part of the spectrum to impress itself, were no mica to intervene. To increase the thickness of the dark mica soon obstructs all rays in the red visible to the eye.

Examined by the thermometric apparatus, a thermopile, and in the radiometer balance—described below—the dark micas which allow any trace of visible rays to pass are strongly diathermic. As the thickness of mica increases the deflection of the index spot of light gets less and less, until there is very little action at all. Judging from analogy it is most probable that as the thickness increases the heat rays are cut off in regular gradation from the line B in the red to the longest rays of heat which will affect the radiometer balance.

This is only a hypothesis and does not take into account the possibility of their being dark bands in the infra-red portion of the heat spectrum. Still the hypothesis as a working tool has been of considerable use, and has helped me to select dark mica obscuring media—giving good and concordant results.

Were I to take at random a piece of black mica which would cut off all the rays visible to the eye, and not allow any red and ultra red rays to pass that would affect the pan-chromatic plate, I should have no certainty that the piece of mica would not cut off some of the heat rays which the glass transmitted. If, on the other hand, I select a piece that allows the red rays near the lines B and C to pass (as shown on the photo-spectrograph), some of the action on the radiometer balance would be due to the luminous red rays, and it is not advisable to entirely cut these off as the residual colour thereby might be affected. The plan ultimately adopted was gradually to increase the thickness of the mica until the photo-spectrograph showed that the visible red had just ceased to affect the plate. After experimenting on some hundred kinds and thicknesses of brown and black mica I succeeded in getting a piece which appeared to satisfy all requirements; the examination of the different kinds of glass made in my laboratory during the last four years has been carried on by help of this specimen.

(To be continued).

FACTORS INVOLVED IN OPENING UP THE FIELD OF UNUSED ELEMENTS.

By CHAS. BASKERVILLE, Ph.D., F.C.S.

Professor of Chemistry and Director of the Laboratory, College of the City of New York.

IN attempting to classify the accepted elements so that one group, or pseudo-group, contains those elements designated "unused" or "little used," one is confronted with many difficulties. The prime difficulties involve the purpose of the classification and the extent of the use. What concerns us this evening is admittedly of technical significance, and must involve economic considerations, yet may not be devoid of abstract scientific interest.

Are we to confine our discussion to the elements or their compounds, or are we to include both? I give herewith a table of "unused" or "little used" elements, whose compounds are used more or less. The periodic classification is followed for convenience. This and two other tables which are given later are confessedly imperfect and based upon capricious opinion, but perhaps may serve our purpose.

Elements Little Used or not Used, but whose Compounds are used More or Less.

0.	1.	2.	3.	4.	5.	6.	7.	8.	Unclas.
	Li	Mg	B	S	As		F	Co	
	K	Ca		Zr			Br		
		Ba		Ce			I		
		Ra		Th					

* "On the Free Transmission of Radiant Heat through Different Solid and Liquid Bodies" (*Ann. de Chim. et de Phys.*, vol. liii., p. 1); Taylor's "Scientific Memoirs" (vol. i., p. 1). "New Researches Relative to the Immediate Transmission of Radiant Heat through Different Solid and Liquid Bodies" (*Ann. de Chim. et de Phys.*, vol. lv., p. 337); Taylor's "Scientific Memoirs" (vol. i., p. 39).

Over one-third of the accepted chemical elements have no serious commercial uses at present as elements or compounds. These are given in the following table:—

Elements or Compounds Unused or Little Used.

o.	1.	2.	3.	4.	5.	6.	7.	8.	Unclas.
He	Rb	Be	Sc	Ge	Cb	Se	Rh	Pr	
Ne	Cs	Sr	Y		Yb	Te	Ru	Nd	
A			La				Os	Sm	
Kr			Ga					Eu	
Xe			In					Gd	
Nt			Er					Dy	
			Tl					Tm	
								Lu	
								Tb	

About one-half of these have been discovered within the last thirty years. Those so recently made known are usually classified under the two groups of "rare gases" and "rare earths." Of the latter it may be well to point out that the group is further conveniently subdivided under the heading of "rare earths" as follows:—

Ce group.		Tb group.		Yt group.	
Element.	Atomic wt.	Element.	Atomic wt.	Element.	Atomic wt.
Sc	44.1	Eu	152.0	Dy	162.5
Yt	89.0	Gd	157.3	Ho	?
La	139.0	Tb	159.2	Er	167.4
Ce	140.25			Th	168.5
Pr	140.6			Yb	172.0
Nd	144.3			Lu	174.0
Sm	150.4				

Your attention is directed to the melting-points and specific gravities of four of them.

Melting-points.

Ce = 623° C.	} Give a rough standard of comparison.
La = 810° C.	
Nd = 840° C.	
Pr = 940° C.	
Al = 660° C.	
Ag = 960° C.	

Specific Gravities.

La = 6.15
Pr = 6.48
Nd = 6.96
Ce = 7.04

Cerium has about the same density as Sn (7.3), but all of them readily oxidise on exposure to air. Cerium is between lead and tin in its physical appearance, and harder than tin, while lanthanum acts much like metallic calcium, its oxide combining readily with water to form the hydroxide, being even air-slaked (combining with carbon dioxide) as does lime. I exhibit here small samples of these metals prepared in my laboratory. In passing I may state that the price of metallic cerium in Germany within a few years has fallen from 250 to 20 marks per kilo.

The word "rare" as applied above—as is the case with so many words of qualification—has changed its meaning in the light of very recent investigations, although the "rare gases" are found in the atmosphere in the following proportions:—

Noble Gases.

Name.	Atomic weight.	1 part by volume in air.
Helium.. ..	4.0	2,450 vols.
Neon	20.0	808 "
Argon	39.9	105 "
Krypton	81.8	746,000 "
Xenon	128.0	4,846,000 "

Some of the elements mentioned above are by no means so uncommon now, and may be had in commercial quantities. I give herewith a table containing these and some

other elements, many of which have been known for a long time, not now used extensively, but inviting application:—

Elements Now Available, or Easily Rendered Available, in Commercial Quantities but Little Used.

o.	1.	2.	3.	4.	5.	6.	7.	8.	Unclas.
A	K	Ca	B	Si	As	Se	Br	Co	
		Sr	Y	Zr	Cb	Te	I	Pd	
		Ba	La	Ce	Ta				
		Cd		Th					

Now that we have seen the field, let us see what are some of the factors involved in bringing it under cultivation. I know how hard the work is. I have been a field hand, for as my old friend President McIver once said, "I've ploughed new ground with a blind mule."

In some cases we lay the lack of use of the elements at once to the scarcity of known occurrences. Haber has shown that osmium is the best catalyser for making ammonia from its elements, but von Welsbach, who devised the osmium filament lamp, has calculated that there are only a few hundred pounds of osmium available in the periphery of our globe. When, however, we remember that carbon is but 0.21 per cent, while silicon is 25.3 per cent of the crust of our earth for a depth of ten miles, including the waters on the earth and its surrounding atmosphere, according to Clarke's calculations, we know that our present utilisation of the elements commercially bears but little relation to their total quantity. With some striking exceptions, man has found more or less ample sources of the elements or their compounds when it has been shown that our civilisation required them. I need but mention tungsten, thorium, vanadium, and radium in illustration. It is not the small percentage in which these elements occur, for palladium exists in nickeliferous pyrrhotites in quantities too small to be detected by even refined chemical analysis, but it accumulates in the slimes of nickel refineries, and is thus obtained in some quantity. The price fixed by possession is the deterrent in the development of the use of palladium, a fact of no individual immorality, perhaps even praiseworthy, but contrary to the law of economics. Some ten years ago one large corporation possessing a store of palladium was approached by some technologists, supported by good repute, with the idea of working out uses for that by-product. The owners said they were not interested in spending a thousand dollars on the investigation—they did not mind spending the money, but they would not be a party to lowering the price of the material in their possession, the inevitable result of extending its use. This principle is well illustrated in the history of metallic aluminium and thorium oxide, whose market quotations have fallen to one one-hundredth and two one-hundredths respectively what they were one generation ago.

On account of its great resistance to atmospheric oxidation and moisture and to the effect of sulphuretted gases, palladium has been employed for the inner mechanism of chronometers and watches, for the construction of fine balance beams, for the divided scales of delicate apparatus, for surgical instruments. It has been used for coating silver goods, and for electroplating searchlight mirrors, for soldering platinum, and in dental preparations. Palladinised asbestos, palladium sponge, and palladium black are most efficient catalytic substances for reducing purposes. This well-known fact may be flashed from the housetops without any fear of coagulating the clouds of litigation hovering over the oil-hardening situation in this country, as the parties referred to still own the palladium.

Some of these "unused" elements will be used, if the prices are made more reasonable. A very important factor in reducing the market prices of these substances is an improvement in methods of extraction. This I may illustrate from the group of rare earths, not that I mean to lead you into that maze, but because it shows how modern tools have served the purpose and gives suggestions for

needed extension with other elements in that class of "meta-elements," as Crookes termed them.

Monazite sand is essentially a phosphate of the rare earths containing variable amounts of thorium, usually 4–6 per cent. The problem of obtaining thorium compounds from that source—315,000,000 Welsbach mantles was the world's output in 1913—depends upon (1) solution, usually by baking, with concentrated sulphuric acid and leaching. Very fine grinding of the sand was essential. (2) The rare earths and thorium are then thrown out as oxalates to remove the last trace of phosphoric acid. (3) The mixed oxalates were brought into solution with the destruction of the oxalic acid, and the thorium precipitated or the oxalates were treated with ammonium oxalate, whereby the nonhydrated thorium tetra-ammonium oxalate went into solution. This thorium salt was subsequently converted into nitrate. Withal the price of thorium salts steadily declined until it seemed to reach a limit.

Muthmann and Weiss conceived the plan of distilling off the phosphorus and converting the metallic elements present into carbides. The resultant mass is hard, and is very expensive to grind in order subsequently to dissolve it. The writer later produced calcium carbide within the mixture of other carbides, using the unground monazite sand. This mass when thrown into water crumbles at once to a powder from which the suspended milk of lime is readily washed. The residual mass of carbides goes into solution in commercial hydrochloric acid from which the thorium may be precipitated at once in a form readily soluble in nitric acid. The cerium may be thrown out of the solution from the thorium precipitates, and tons of oxalic acid are now destroyed or locked up in the by-product of rare earths which are accumulating awaiting the development of uses.

Muthmann and Weiss and Hirsch in this country have applied the Hall process for the isolation of metallic cerium, whose use is now practically limited to pyrophoric alloys.

Very recently it has been proven to be distinctly profitable, according to separate patents of Soddy and Hahn, to separate meso-thorium compounds in the process of extracting and purifying the thorium. Meso-thorium rivals radium in some of its applications in radio-surgery.

The three instances cited above are given for another reason. The ideas were worked out by three college professors. Labourers must be provided for clearing the field, whether the toil be that of working out new processes to so reduce the cost of a material as to admit of its application or to develop uses not known for by-products now quoted at fictitious prices, but which do not appear at such supposititious values in the annual financial statement.

Undoubtedly the best way to work out problems of the utilisation of "undeveloped elements" is to attack them in such well-equipped and splendidly manned research laboratories as are maintained by the General Electric Co., the General Chemical Co., the Eastman Kodak Co., and others, but their up-keep involves large expenditures. Many college and university professors would welcome a subsidy for work of this character, which should be scientific, dignified, and help keep the wolf from the door. I commend for your amusing perusal "The Confessions of a College Professor's Wife" in a recent number of the *Saturday Evening Post*. I do not mean that the college professor is prepared to or should go into the factory, but he can work at an idea which should later be developed, if it has merit, on a commercial scale by the technical chemist or chemical engineer. Elaboration of this proposition, which is not novel with the speaker, is not necessary here. Suffice it to say that one so selected would bring to the problem a degree of ignorance that might be stimulating and a freedom from tradition which would admit of a display of imagination necessary to utilise material which is commercially abundant and inviting investigation.

H. B. Baker has said somewhere:—"Nothing can be of more value to science than the exhaustive study of one

particular action." Weiss and Neumann have found that compressed zirconium is a conductor, whereas previous statements have been that it was non-conducting. There is need of reviewing many such statements that are handed down in the literature. Aluminium is sonorous according to so many text-books. I have a sample of very pure aluminium, a part of which was used by the late Prof. Mallet in the determination of its atomic weight, and, as he assured me, it is not sonorous. If aluminium is sonorous it is not pure. Although I have been informed that this statement is not true, if the aluminium has been rolled.

Stewart, in his charming book on "Recent Advances in Physical and Inorganic Chemistry," in referring to 1887 and the following years of feverish activity in physico-chemical research, led by Arrhenius, van 't Hoff, and the elder Ostwald, says:—"To some extent this wave appears to have spent its force. At the present day physical chemistry, except in the hands of a few exceptional researchers, has degenerated into a means of attacking the problems of pure chemistry instead of opening up new fields; and consequently there is a certain tendency to decry the subject as a mere means to an end, and not a living branch of science. This is perhaps an exaggerated view; but it cannot be denied that physical chemists of the present day are not animated by the high hopes which seem to have inspired Ostwald and others in the earlier days of the subject." Bancroft acknowledges that there is some truth in this criticism, but asserts:—"The difficulty is that most people are still struggling under the limitations imposed deliberately and consciously by Ostwald. Once these are broken through, nobody will have any cause to complain of the wave having spent its force." Stewart further says:—"It is an extremely fortunate coincidence that as the first movement declined, a second and perhaps more powerful one had succeeded it. This second movement rose with even greater rapidity than pure physical chemistry, and yet at the present day we appear to have touched only the fringe of the subject of radio-activity; so that we may look forward to a long career of fruitful investigation still before us in this department of chemistry."

The problems of sub atomic or electronic universe have presented themselves, and at once we begin applying these new ideas to utilitarian purposes. The cryogenic laboratories have accumulated fractions from tons of liquefied air. Collie found that neon thus had incidentally luminesces under the influence of the Hertzian waves. A tube of neon serves as a detector of the nodes and loops, glowing brilliantly under the influence of the latter as if it were excited by an induction coil. Tubes of neon, prepared by Claude in Paris, electrically excited, offer a most pleasing and perhaps later on may supply an economical form of artificial light approaching sunlight.

Quantities of argon are now available from liquefied air. There are indications that, on account of its inertness, we may shortly see tungsten incandescent lamps, as Whitney puts it, with "the vacuum jar full of argon" instead of nitrogen. Troost and Ouyard have stated that they have succeeded in causing argon to combine with magnesium vapour. Neither Rayleigh, Ramsay, nor Moissan were able to secure any evidence of the formation of compounds of argon, however. Many reactions unobserved on the laboratory scale are found to occur when dealing with large quantities of substances through long periods of time. If this were not true we should have even greater difficulty in accounting for the occurrence of such inert gases as helium in malacome, clevite, and thorianite. If it is thus barely possible that in time we shall find compounds of argon produced in the large scale operations of burning the nitrogen of the air, as carried on so successfully in Norway at present. A use of compounds of argon may then be found.

The development of radio-activity has projected us into an undreamed of realm of thought and new interests. The phenomena of radiology are closely allied to those of radio-activity. The use of Röntgen rays in medicine has

been attendant with not a few difficulties. Among them the so-called "hardness" and "softness" of the rays. The former are the penetrating and affect tissues, sometimes favourably and sometimes unfavourably, far below the surface. The "soft" rays affect the epidermis. In the use of "hard" X-rays tubes for deep treatment it is necessary to screen the skin with various thicknesses of aluminium or lead, &c. For treatment of skin affections only, there have been no satisfactory means for screening out the penetrating rays, consequently the problem has been the production of "soft" rays with a minimum of "hard" rays. X-ray tube glass is usually a potash or soda-lime silicate. Lindemann found that by substituting lithium for potassium the rays were "softer." He then substituted beryllium for calcium, and finally boron for silicon. Lithium-beryllium-boron glass shows over 30 per cent reduction in the empirical molecular weight. Windows of this glass let into X-ray tubes give the "soft" rays desired. I am pleased to exhibit, through the courtesy of Waite and Bartlett, one of these tubes wherein three "unused" elements were utilised. It would be interesting to see the effect with a potassium-barium-zirconium glass. We know the effect of substituting tungsten for the platinum target within these tubes.

In connection with the above I show you samples of titan-quartz and zircon-quartz glass, for which original properties are claimed. Analyses of such quartz published in the *Chemiker Zeitung* show from 0.05–0.15 per cent of zirconium, and 0.0–0.11 per cent of titanium oxide, so they are what they are not.

Application of the newer electronic conceptions of valence, especially when associated with residual affinity, with the development of methods for changing valence according to our wishes, will unquestionably cause many of these unused elements and many of those now most used to assume new properties. I call your attention to one qualitative illustration. Pure lead does not plate on iron. When molten lead is caused to flow to and fro as a conductor of a low voltage high ampère alternating current for variable periods of time, usually several hours, it then plates iron as may be seen from the sample so plated this week. The lead is pitted and the sample not perfect, but it points a way, which may serve as a hint in seeking uses for such elements as cadmium, selenium, and tellurium.

An indifferent and unsatisfying classification of the "unused" elements has been attempted. Over one-third of the accepted chemical elements are little used. "Rare" elements have been shown to be not so rare. Furthermore, rarity bears little direct relationship to utility. Desire to eat the cake and keep it at the same time are important factors in making use of some of the elements. Illustrations of the development of methods for reducing the cost of production have been cited. Means for stimulating work in utilising elements now available have been suggested. These workers at least could correct much of the misinformation now transmitted by the normal channels from one generation to another. Directions in which real modern physical chemistry has made it possible to use some of these elements and opened up further possibilities have been mentioned. The limited time and assumed patience of our members have forced a degree of unavoidable superficiality.

The Seventh Congress of the International Association for Testing Materials will be held under the Patronage of H.M. the Czar of Russia, in St. Petersburg, from August 12–17, 1915. Four days will be devoted to the discussion of the most important problems on testing materials. After the Congress extensive excursions in the interior of Russia have been arranged. The Offices of the British Section of the Association are at the Iron and Steel Institute, 28, Victoria Street, London, S.W.

CHEMICAL REACTIONS AT VERY LOW PRESSURES.*

—THE CLEAN-UP OF OXYGEN IN A TUNGSTEN LAMP.

By IRVING LANGMUIR.

(Concluded from p. 257).

Summary.

1. In order to obtain a vacuum so free from water-vapour that a heated tungsten filament will not produce appreciable quantities of hydrogen by the decomposition of the water-vapour, it is necessary during exhaustion to heat the bulb to 360° for about an hour, and to employ either phosphorus pentoxide or liquid air as a drying agent.

2. By this heating about 300 cu. mm. of water-vapour, 20 cu. mm. of carbon dioxide, and 4 cu. mm. of nitrogen are evolved from a 40 watt lamp bulb which could not be removed from the bulb at room temperature by ordinary means.

3. A tungsten wire heated in oxygen at low pressures begins to oxidise at about 800° K, the oxide forming a brown or blue coating on the metal. By heating to about 1200° the oxide volatilises without dissociation and leaves the wire clean and bright.

4. Above 1200° oxygen at pressures below 0.02 mm. acts on a tungsten wire at a rate which is strictly proportional to the pressure of oxygen and is proportional to the surface of tungsten exposed. The rate increases as rapidly with the temperature as do the rates of most chemical reactions at similarly high temperatures. No fatigue effect can be observed, and the past history of the wire does not influence the results. There is much evidence that no film of oxide remains on the metal, but that the oxide distils off to the bulb as fast as formed.

5. The composition of the oxide produced is WO_3 .

6. The velocity of the reaction is not affected by varying the temperature of the bulb.

7. The conditions under which this reaction was studied differ in several important respects from those that prevail with reactions at ordinary pressures. Because of the fact that the normal free path of the molecules of the gas is of the same order of magnitude as the dimensions of the bulb, the following unusual conditions prevail:—

(a) A molecule of oxygen can strike the filament only once before returning to the surface of the bulb.

(b) The velocity of the oxygen molecules is not affected by the temperature to which the filament may be heated. Hence we may say that the metal is made to react with a gas at a totally different temperature from itself—a thing impossible at atmospheric pressure.

(c) The product of the reaction, WO_3 , in diffusing away cannot influence the rate at which the oxygen comes in contact with the metal, as would be the case at higher pressures.

These facts make it much easier to study the mechanism of the reaction.

8. The rate at which the oxygen molecules come into contact with the surface of the filament was calculated. This rate gives the maximum possible rate of the chemical reaction. The ratio of the actually observed rate to this maximum rate is called ϵ . The values of ϵ at different temperatures are given in Table IV. They range from 0.0011 at 1270° K to 0.15 at 2770° K.

9. Applying the principles of the kinetic theory to an analysis of the experimental data, we are led to the following conception of the mechanism of the reaction:—

The oxygen molecules that strike the filament do not react directly with tungsten atoms, but as a first step become negatively charged by taking up an electron from the metal. On the average about 30 electrons in the metal collide with the oxygen molecule during the time that it is in contact with the metal. Only those electrons which

* Paper read before the New York Section of the American Chemical Society. From the *Journal of the American Chemical Society*, xxxv., No. 2.

have a velocity of 62×10^6 cm. per sec. or more succeed in charging the oxygen atoms. When we say that 30 electrons collide with each oxygen molecule, we mean that 30 electrons reach such positions with respect to the oxygen molecule that they would combine with it if their velocities were greater than 62×10^6 cm. per sec. The number of electrons in the metal that have velocities as high as this is so small that only a few of the oxygen molecules that strike the tungsten become negatively charged. For example, with the tungsten wire at 1270° , only one electron out of about 24,400 has a velocity as high as 62×10^6 . Therefore the number of oxygen molecules that receive a charge is only $30/24,400$, or only about one out of a thousand.

The number of electrons in the metal must be at least one-seventh as great as the number of tungsten atoms.

The oxygen molecule, after taking up a negative charge, is held by electrostatic forces to the positively charged tungsten atoms, and soon, by secondary reactions, combines with the tungsten and with oxygen atoms to form WO_3 . The present experiments do not throw much light on the nature of these secondary reactions.

This theory accounts quantitatively for the observed values of ϵ between the temperatures 1270 and 1770° K, and for the fact that ϵ does not depend on the temperature of the oxygen. It also leads to several interesting deductions which do not appear to be inconsistent with known facts.

The writer wishes to express his indebtedness to Mr. S. P. Sweetser, who has carried out most of the experimental part of this investigation.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 21, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Effect of the Magnetron in the Scattering of α -Rays." By Prof. W. M. HICKS, F.R.S.

The presence of a magnetron in an atom must exert some effect in scattering α - or β -particles passing through the atom. In order to test the order of magnitude of the effect, the orbits of charged particles moving in the equatorial plane of a magnetron are discussed, and it is seen that the scattering produced is very considerable. The nearest approach of an α -particle to the centre of the atom is of the same order as in Rutherford's theory. The electrostatic repulsion of an α -particle combined with the magnetic field of the atom will therefore be more effective, as the diminished velocity will render the particle much more susceptible to the magnetic forces.

"Luminous Vapours Distilled from the Arc, with Applications to the Study of Spectrum Series and their Origin." (I.). By the Hon. R. J. STRUTT, F.R.S.

1. It is known that mercury vapour distilled away from the arc *in vacuo* remains luminous for some distance away from the region of discharge. It is now shown how to observe brilliant effects of the same kind from a large number of other metals.

2. As the luminous vapour moves away from the region of discharge, the rate at which different constituents in the spectrum die out is not always the same. Thus, for instance, both the subordinate series of lines in the sodium spectrum die out at the same rate, but the principal series dies out more slowly. The lines belonging to any given series always die out at the same rate, but another series may or may not die out at the same rate as the first.

3. In some cases the glowing vapour distilled from the arc shows a band spectrum. The alkali metals show a continuous band beyond the limit of the subordinate series like that seen in absorption in the hydrogen stars.

The present instalment of this investigation deals only with experimental methods of observing the luminous jets of metallic vapour distilled from the arc and their more obvious features. In the next I hope to discuss the effect of an electric field in quenching the luminosity, and the inferences which can be drawn from the observations generally as to the origin of the radiation and its various spectroscopic constituents.

"On the Ionisation of Gases by Collision and the Ionising Potential for Positive Ions and Negative Corpuscles." By W. T. PAWLOW.

"The Determination of Elastic Limits under Alternating Stress Conditions." By C. E. STROMEYER.

The present paper deals exclusively with the question of Endurance or Fatigue qualities of metals. The apparently incongruous results obtained by previous experimenters, including those by Wöhler, made it appear probable that samples taken from different parts of a bar or plate might differ so much in quality that the law of fatigue would be masked by local variation of quality. The test pieces of the present first series (*bending*) were therefore shaped in such a manner that consecutive pieces were separated from each other in the original plate by only one inch. The test results were found to be very consistent and could be expressed by the formula $S_n = Fl + C(10^6 : N)^{1/4}$, where S_n is the nominal alternating stress which will cause fracture after N repetitions, Fl is the fatigue limit found by extrapolation from a series of tests resulting in fracture, and C is a constant. A comparison was made of previous tests with the help of this formula, and it was found to agree well with those of Wöhler, Baker and Eden, Rose and Cunningham.

The torsion fatigue tests were made with the same materials as used in the above tests, and the results also agreed very closely with the above formula, except that new values for Fl and C were found. A comparison was made between the fatigue limits as found by the bending-fatigue tests and by the torsion-fatigue tests, the ratio between the two averaging about 3 to 2. The comparison between the bending and shearing stresses, which will produce fracture after a certain number of revolutions, has also been made, but is of relatively less value, for these stresses are merely nominal ones and the formulae which would reduce them to actual stresses are not the same for bending as for torsion.

The enquiry was extended to the measuring of the heat generated during fatigue tests. It was found that with low alternating stresses no heat was produced, or, at any rate, so little that it could not be measured, but when certain limiting stresses were exceeded then the generation of heat was quite perceptible. The stresses, at which there was a first indication of heat production, were assumed to be the fatigue limits of the material, for the heat production suggests internal friction and these limits agreed reasonably well with the fatigue limits (Fl) which were found by extrapolation with the help of the above formula.

This calorimetrically-determined fatigue limit was practically a fixed value for any one quality of material, the most interesting case being a crank shaft from which 19 samples were cut. In the first group of three samples cut from the end of the shaft, the minimum and maximum values of the fatigue limit were 11.15 and 11.40 tons per sq. in. In the second group of eight samples cut from between the crank webs, the fatigue limits ranged from 11.30 to 11.60 tons per sq. in., and in the third group of eight samples they ranged from 12.05 to 12.15.

These results agree amongst themselves far better than the tensile tests of the same material, tests which at present are looked upon as reliable indicators of quality.

"The Emission of Electricity from various Substances at High Temperatures." By G. W. C. KAYE and W. F. HIGGINS.

Experiments have been conducted at temperatures from 2000° to 2500° C. within a carbon-tube furnace at atmospheric pressure. Under these conditions the electrical emissions, in the absence of any applied potential, have been measured for a number of substances (including the alkaline earths and the metals tin, aluminium, iron, and copper) on their introduction into the furnace. During their rapid volatilisation the substances gave out large amounts of electricity which, with one exception, were negative in sign. For example, barium oxide and alumina generated negative currents of the order of 4 ampères per sq. cm., boiling tin about 2 ampères per sq. cm., and boiling iron about 1 ampère per sq. cm. Boiling brass, on the contrary, produced a positive current of about 0.5 ampère per sq. cm. The results have interest in connection with the problems of solar magnetism. Incidentally, striking absorption-colourations of the emitted light from the furnace were observed when the alkaline earths were introduced, e.g., the colour in the case of strontia was a brilliant green, and with baryta a salmon-pink.

CHEMICAL SOCIETY.

Ordinary Meeting, May 7, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President,
in the Chair.

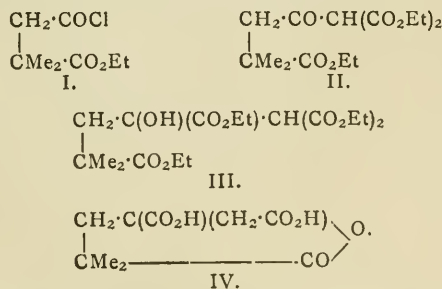
(Concluded from p. 235).

129. "The Alloys of Aluminium and Silicon." By CHARLES EDWARD ROBERTS.

A re-investigation of the thermal diagram of the aluminium-silicon alloys in order to determine the possibility of the existence of either a compound of the two elements dissociating at high temperatures on an allotropic form of silicon stable above 1200°, resulted in a complete confirmation of the results arrived at by Fraenkel (*Zeit. Anorg. Chem.*, 1908, lvi., 154), that the alloys form a simple eutectiferous series, the eutectic melting at 578°.

130. "The Constitution of Camphene. Part II. Experiments on the Synthesis of Several Degradation Products of Camphene." By WALTER NORMAN HAWORTH and ALBERT THEODORE KING.

An account was given of the condensation of ethyl oxalate with ethyl *as*-dimethylsuccinate in the presence of potassium or sodium ethoxide, and of the synthesis of the lactic acid (IV.) through the following stages:—



Attention was directed to the fact that a complete synthesis of camphene has now been realised by the combined experiments of several independent workers. Camphenic acid and camphenilone having now been synthesised (*Ber.*, 1914, xlvii., 871, 934), this, considered along with the earlier work of Moycho and Zienkowski (*Ber.*, 1905, xxxviii., 2461; *Annalen*, 1905, cccxi., 58) on the preparation of camphene from camphenilone, establishes finally the constitution of this terpene as represented by Wagner's formula.

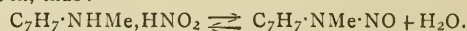
131. "Action of Nitrous Acid on Dimethylpiperazine." By PRAFULLA CHANDRA RAY.

In continuation of previous investigations on the amine nitrites, attempts have been made to isolate an amine dinitrite. When ethylenediamine hydrochloride or hydrobromide was treated with silver nitrite, it was noticed that even during the initial stages of reaction slight decomposition often set in, with evolution of nitrogen and formation of glycol and ethylene oxide. The aqueous filtrate, on evaporation in a vacuum, gave a non-crystalline residue, which did not dissolve to a clear solution, and on evaluation by the Crum-Frankland and "urea" methods respectively, gave, as a rule, an appreciable excess of gas by the former, proving the conversion of a certain proportion of nitrite into nitrate. In two preparations, however, the nitrogen, as estimated by both the processes, agreed well:—

1. 0.0214 gave 2.1 cc. N₂ ("nitritic") at 24° and 760 mm. N = 11.0.
2. 0.025 gave 2.6 cc. N₂ ("nitritic") at 25° and 760 mm. N = 11.34.

The result approximates to a mononitrite, C₂H₄(NH₂)₂.HNO₂, which requires N ("nitritic") = 13.08 per cent. That the percentage of nitrogen actually found is lower is easily accounted for by the fact that there is always a slight insoluble residue.

It has already been shown (*Proc.*, 1912, xxviii., 258) that whilst benzyethylammonium nitrite can be isolated in a crystalline form, the corresponding methyl compound decomposes even in aqueous solution, mainly into the nitroso-derivative, and that after some time equilibrium sets in, thus:—



It has now been found that by using an alcoholic solution of the amine hydrochloride, this reverse change is completely arrested. The alcoholic solution, when evaporated in a vacuum over sulphuric acid, yields a crystalline mass, which is benzyethylammonium nitrite:—

- 0.0294 gave 2.45 cc. N₂ ("nitritic") at 33° and 760 mm. N = 8.94.

C₈H₁₁N.HNO₂ requires N = 8.33 per cent.

An alcoholic solution of piperazinium chloride, when similarly treated, gave a salt approximating to a dinitrite. It was thought that dimethylpiperazine might yield better results, and this expectation has been realised. The base chosen was *a*:2:5-dimethylpiperazine, which Pope and Read's recent investigations prove to have the *trans*-configuration (*Trans.*, 1912, ci., 2325; 1914, cv., 219).

The aqueous solution of the hydrochloride, on treatment with silver nitrite and evaporation of the filtrate in a vacuum, gave a crystalline salt, which was found to be nitrosodimethylpiperazinium nitrite,—



0.0286 gave 7.3 cc. NO at 26° and 760 mm. by the Crum-Frankland method, whereas the "urea" test liberated only half the amount of nitrogen (compare *Trans.*, 1913, ciii., 2), whence N = 14.66.

C₆H₁₃ON₃.HNO₂ requires N = 14.74 per cent.

It should be mentioned that the aqueous solution of piperazinium chloride, by treatment as above, gave dinitrosopiperazine in the first two or three crops. The introduction of the two methyl groups in the ring had the desired effect of diminishing the tendency towards the formation of the nitroso-derivative.

Dimethylpiperazinium chloride in alcoholic solution was next treated with finely powdered silver nitrite. Although both the reacting substances are very sparingly soluble in alcohol, the increased solubility of silver nitrite in the presence of an amine nitrite (due, no doubt, to the formation of a double salt) facilitates the double decomposition. The alcoholic filtrate was evaporated in a vacuum, and the crystalline salt which was thus obtained was found to be a dinitrite, as both by the Crum-Frankland and the "urea" process it yielded the same amount of nitrogen:—

0.023 gave 2.7 cc. N_2 ("nitric") at 30° and 760 mm.
N = 13.33.
0.0764 (by combustion) gave 18.0 cc. N_2 at 26° and 760 mm. N = 26.41.
 $C_6H_{14}N_2 \cdot 2HNO_2$ requires N ("nitric") = 13.46, and N (total) = 26.92 per cent.

Conductivity measurements also bear out that the one is the nitrite of a nitroso-derivative and the other a dinitrite (compare *Trans.*, 1912, ci., 1555).

Nitrosodimethylpiperazinium Nitrite.

V	252.1	504.2	1008.4	2016.8
μ	93.5	102.7	114.3	120.7

In this case there are only two univalent ions.

Dimethylpiperazinium Dinitrite.

V	200.3	400.6	801.4	1602.4
μ	210.3	225.4	237.2	241.1

Evidently there are three ions in solution. The measurements were conducted at 25°.

132. "Partially Methylated Glucoses. Part III. Monomethyl Glucose." By JAMES COLQUHOUN IRVINE and THOMAS PERCIVAL HOGG.

Monomethyl glucose has been prepared from glucose-diacetone on a sufficiently large scale to permit of the α - and β -modifications being isolated in pure stereochemical forms. As the interconversion $\alpha \rightleftharpoons \beta$ proceeds extremely slowly in pure methyl alcohol, it has been possible to determine the initial specific rotation of each form of the sugar with a high degree of accuracy. The mutarotatory changes observed were:—

α -Form (m.p. 160.5—161°). β -Form (m.p. 133.5—135°).
Initial $[\alpha]_D + 107.6^\circ \rightarrow 68.5^\circ, 68.3^\circ \leftarrow + 24.4^\circ$ initial $[\alpha]_D$.

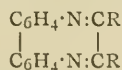
The difference of the molecular rotations of the α - and β -forms thus equals 161.41, and as the corresponding value for glucose is 16200, the result agrees with Hudson's rule (*Journ. Am. Chem. Soc.*, 1909, xxxi., 66) within the limits of experimental error.

It has been found that monomethyl glucose yields few characteristic derivatives, and its methylglucosides, in view of the spatial distribution of the hydroxyl groups, fail to enter into condensation with either acetone or benzaldehyde. A well defined monomethyl glucoseanilide was, however, isolated (m. p. 154—155°). This compound shows suspended mutarotation in a remarkable degree, and the optical change $[\alpha]_D - 108.5^\circ \rightarrow -50.3^\circ$ was only promoted by traces of acids, and not by alkalis.

The constitution previously assigned to monomethyl glucose has been confirmed, as, on oxidation with nitric acid, the sugar is converted into monomethyl gluconolactone, thus indicating that the methoxyl group is attached to a terminal carbon atom. The sugar is not fermented by living yeast, or by yeast extract, and is unaffected by most bacteria which attack glucose. The action of *B. Cloacae* (Jordan), however, resulted in the formation of both acid and gas, but the reaction proceeded much more slowly than in the case of glucose.

133. "Studies in the Diphenyl Series. Part VI. The Configuration of Diphenyl and its Derivatives." By JOHN CANNELL CAIN and FRANCES MARY GORE MICKLETHWAIT.

It has been found that benzidine and tolidine condense with reagents for ortho-diamines, such as benzil and glyoxal, to form compounds of the type—



(where R = H or C_6H_5).

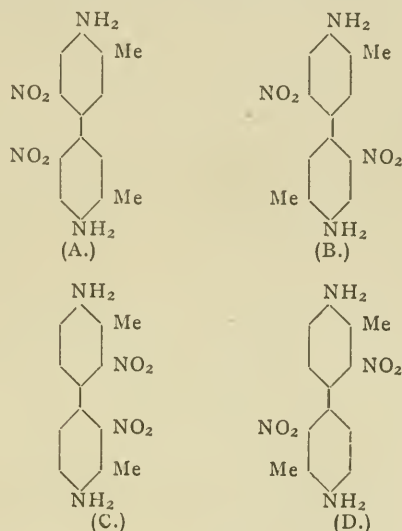
This reaction appears to prove that Kaufler's stereochemical configuration of members of the diphenyl series is correct.

134. "Studies in the Diphenyl Series. Part VII. Isomeric o- and m-Dinitro-o-tolidenes." By JOHN CANNELL CAIN and FRANCES MARY GORE MICKLETHWAIT.

In addition to the o-dinitrotolidine (m. p. 270°) described by Gerber, the authors have obtained, by the nitration of diacetylitolidine, a new isomeric o-dinitrotolidine (m. p. 202—203°).

By the nitration of tolidine sulphate or diphtalyltolidine there are formed in addition to Gerber's m-dinitrotolidine (m. p. 217°; obtained by him from tolidine sulphate), three new m-dinitrotolidines, melting at 205—206°, 263°, and 284° respectively.

These four bases are represented by the plane formulæ:—

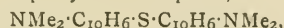


and the possibility of the separate existence of A and B and of C and D, as well as of the two isomeric o-dinitrotolidines, is readily explained by means of Kaufler's stereochemical formula for diphenyl.

135. "Thio-derivatives of β -Naphthylamine." By WILLIAM REEVE and SAMUEL SMILES.

The substances here described were obtained in some experiments which had been undertaken with the object of synthesising $\alpha\beta$ -naphthathiophen. The results are now published, since the scheme has been abandoned on account of the extremely poor yields of the essential products.

Dimethyl- β -naphthylamine sulphide.—



was obtained by treating three molecular proportions of dimethyl- β -naphthaline dissolved in light petroleum with one molecular proportion of sulphur chloride. The insoluble hydrochloride of dimethyl- β -naphthylamine separated, and when this had been removed the required substance was isolated by spontaneous evaporation of the solution. After recrystallisation from hot alcohol it was obtained in very pale yellow needles, which melted at 145°:—

Found, S = 8.4. N = 7.2.

$C_{24}H_{24}N_2S$ requires S = 8.6; N = 7.5 per cent.

Di- β -naphthylamine sulphide, $NH_2 \cdot C_{10}H_6 \cdot S \cdot C_{10}H_6 \cdot NH_2$, was obtained by treating β -naphthylamine in nitrobenzene solution at 160° with sulphur in the presence of lead oxide. The solvent was removed in a current of steam, and the residue was dissolved in acetic acid. Water was then added to this solution, and the amorphous precipitate which separated was collected and dissolved in ether. By spontaneous evaporation of the solvent the sulphide was deposited in an impure condition. It separated from solu-

tion in hot alcohol in colourless needles, which melted at 166° :—

Found, S = 10.0 and 9.8. N = 8.6 and 8.7.

$C_{20}H_{16}N_2S$ requires S = 10.1; N = 8.86 per cent.

When dissolved in hot aqueous mineral acids, the substance was readily oxidised by atmospheric oxygen, an insoluble blue material being formed.

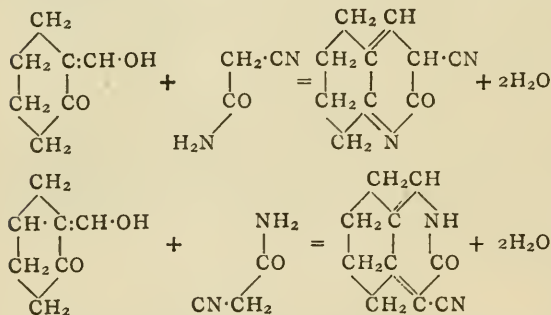
The yield of the sulphide obtained by this method varies considerably, not only according to the quantity of the reagents taken, but also according to other conditions, which have not yet been determined. In the majority of experiments the yield was extremely poor, and in these cases it is difficult to separate the substance from the polysulphides which are always formed. These compounds—the di- and tri-sulphides—have not been closely examined.

136. "The Interaction of Naphthasulphonium-quinone and Substances containing the Thiol Group." By BROJENDRANATH GHOSH and SAMUEL SMILES.

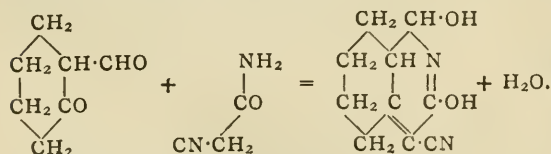
A description was given of the reaction of certain thiol derivatives with β -naphthaquinone and β -naphthasulphonium-quinone. From the last-named quinone, thiol and thioglycolyl derivatives of dinaphthathioxin were obtained. The action of alkali with these substances and with hydroxydinaphthathioxin was examined in order to determine whether isomeric change could be induced, as in the case of the isosulphide of β -naphthol. The results were negative.

137. "The Formation of Heterocyclic Compounds from Hydroxymethylene Ketones and Cyanoacetamide." (Preliminary Note). By HEMENDRA KUMAR SEN-GUPTA.

Hydroxymethylene-ketones condense readily with cyanoacetamide in the presence of piperidine or diethylamine, giving rise to heterocyclic compounds; in the case of open-chain hydroxymethylene-ketones, hydroxypyridine derivatives are obtained, whilst with hydroxymethylene-cycloketones, substances are produced which may be either quinoline or isoquinoline derivatives, according as to whether the condensation commences at the formyl carbon atom or the ketonic carbonyl of the hydroxymethylene compound.



In addition to these condensation products which are formed by the elimination of two molecules of water, there is evidence of the formation of a second type in which only one molecule of water is eliminated:—

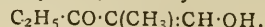


In some cases, this intermediate type has been isolated by careful crystallisation. Since a well-defined acid is obtained by hydrolysing either of the condensation products thus produced, there is little doubt as to the similarity of their structures. In a few cases the final products which are deposited from the condensing mixture have

found to be those condensation products which have lost two molecules of water.

The following compounds have been obtained:—

1. Ethyl hydroxymethylene-ethyl ketone,—



gives with cyanoacetamide a mixture of condensation products which, on hydrolysing, yields an acid, $C_9H_{11}O_3N$ (m. p. $278-279^{\circ}$); this evolves carbon dioxide on melting, and passes into the compound, $C_8H_{11}ON$ (m. p. $136-138^{\circ}$).

2. Hydroxymethylene-cyclohexanone yields the condensation products $C_{10}H_{10}ON_2$ (m. p. 250°) and $C_{10}H_{12}O_2N_2$ (melting above 300°). Both compounds, on hydrolysis with 80 per cent sulphuric acid, give the same acid, $C_{10}H_{11}O_3N$ (m. p. 265°), which evolves carbon dioxide on melting, and passes into the compound, $C_9H_{11}ON$ (m. p. 204°).

3. 2-Methylhydroxymethylene-cyclohexanone gives the compound $C_{11}H_{12}ON_2$ (m. p. 242°), which, on hydrolysis, yields the acid, $C_{11}H_{13}O_3N$ (m. p. 260°); this loses carbon dioxide, and forms the compound, $C_{10}H_{13}ON$ (m. p. 142°).

4. 4-Methylhydroxymethylene-cyclohexanone gives the compound, $C_{11}H_{12}ON_2$ (m. p. $228-229^{\circ}$), which is hydrolysed to the acid, $C_{11}H_{13}O_3N$ (m. p. 284°), and the latter yields the compound, $C_{10}H_{13}ON$ (m. p. $206-207^{\circ}$), with loss of carbon dioxide.

Experiments with the object of elucidating the constitution of this class of compounds are in progress.

138. "Studies of Ammonium Solutions." A Correction. By ROLAND EDGAR SLADE.

In a former communication it was shown that the potential of an ammonium electrode at 25° was given by the equation—

$$e = e_0 - 0.059 \log \frac{p_{NH_3} p_{H_2}^{\frac{1}{2}}}{[NH_4^+]}$$

The value of e_0 was calculated to be -0.486 volt from twelve independent measurements. It has been pointed out to the author by Prof. Auerbach that, in calculating these values of e_0 , the pressures of ammonia were, by mistake, expressed in mm. of mercury instead of in atmospheres. This mistake has now been corrected, and the values have been revised in accordance with the later value for the potential of the normal hydrogen electrode. The revised value of e_0 is -0.654 volt.

This value has been compared with other data, and found to be in excellent agreement.

139. "Thujin." By ARTHUR GEORGE PERKIN.

Rochleder and Kawalier (Wien. Akad. Ber., 1858, xxix., 10; Journ. Pr. Chem., 1858, lxxiv., 8) isolated from the arbor vitae (*Thuja occidentalis*) in minute amount a glucoside, thujin, $C_{20}H_{22}O_{12}$, which by hydrolysis yielded dextrose and thujigenin, $C_{14}H_{14}O_7$, the latter subsequently passing into thujetin, $C_{14}H_{14}O_8$. Thujigenin and thujetin are described as yellow crystalline substances, soluble in alkalis with a green colour, and in alcoholic ammonia with a bluish green coloration. A re-examination has now shown that thujin is, in reality, quercitrin contaminated with a trace of a second glucoside, and that the green tint of the alkaline solution of the free colouring matter originates from the latter compound. It is possibly a glucoside of myricetin (*Trans.*, 1899, lxxv., 829), but the amount present in the material now examined was far too small for identification. Incidentally, it has been found that quercitrin melts at $183-185^{\circ}$, much higher than has been usually supposed (compare Herzig, Monatsb., 1885, vi., 877), that the formula $C_{21}H_{20}O_{12}$, assigned to it previously, which it is found to possess when dried in the air or at 100° , is, in reality, $C_{21}H_{20}O_{11} \cdot H_2O$, and that it may be obtained in the anhydrous condition when heated at 160° .

140. "The Rotatory Powers of d- and l-isoamarine and of their Respective Tartrates." By HENRY LLOYD SNAPE.

In a previous paper on "Racemic and Optically Active Forms of Amarine" (*Trans.*, 1900, lxxvii., 784; see also

Proc., xxx., 7), the density was inadvertently omitted in the calculation of rotatory powers. Re-determinations were subsequently made, and the missing factor was included. As before, the bases were dissolved in ethyl acetate, and the tartrates in 90 per cent alcohol.

Each determination of the angle of rotation was made by taking the average of a number of rotations (which fluctuated slightly and irregularly—sometimes falling and then rising, and sometimes conversely) measured at the same time on successive days. The following are the results obtained:—

	α .	$[\alpha]_D$.	Number of determinations.
Dextro-base ($C_{21}H_{18}N_2$) ..	4'500	+69'06	3
Lævo-base	4'581	-68'23	2
Dextro-tartrate of dextro-base	1'357	+113'95	2
Dextro-tartrate of lævo-base	3'377	-93'31	3

As the only polarimeter which was at the author's disposal for the above experiments was a very simple one, and could not be trusted to give very exact measurements, Prof. W. J. Pope very kindly undertook to determine $[\alpha]$ in specimens of the dextro-tartrates of *d*- and *l*-isoamarine, and the following are his results, for which the author desires to express his thanks.

In each of the following determinations the quantity of the substance stated was dissolved at 20°, made up to 30 cc., and the solution examined in a 4-dcm. tube at 20°.

d-isoamarine *d*-tartrate, 0.9053 grm. in absolute alcohol.

	Hg violet.	Hg green.	Hg yellow.	Na yellow.
α ..	+32'57°	+16'56°	+14'18°	+13'48°
$[\alpha]$	+270	+137	+117	+112

Rotatory dispersions—

Hg violet/Na yellow ..	..	..	=	2'416
Hg green/Na yellow ..	..	..	=	1'228
Hg yellow/Na yellow ..	..	..	=	1'052

0.3097 in 90 per cent alcohol by weight.

	α ..	+12'34°	+6'29°	+5'38°	+5'12°
$[\alpha]$		+299	+152	+130	+124

Rotatory dispersions, 2'410, 1'229, and 1'051 respectively.
1 isoamarine *d*-tartrate, 0.2390 grm. in absolute alcohol.

	α ..	-7'55°	-3'68°	-3'15°	-3'07°
$[\alpha]$		-237	-115	-98.8	-96.3

Rotatory dispersions, 2'459, 1'199, and 1'026 respectively.

It will be observed that the corrected values for the *D* line for the tartrate of the dextro-base in 90 per cent alcohol is 124, which is distinctly higher than was obtained with the imperfect apparatus. Similarly, the value for the tartrate of the lævo-base in absolute alcohol is somewhat higher than was obtained from a solution in 90 per cent alcohol. Probably, therefore, the values given above for the bases are, like those cited in the same table for the tartrates, only approximately correct.

NOTICES OF BOOKS.

The Viscosity of Liquids. By A. E. DUNSTAN, D.Sc. (Lond.), and F. B. THOLE, B.Sc. (Lond.). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

THE authors of this monograph have done a useful work to science in bringing together the scattered data relating to the measurement of the viscosity of liquids. A good deal of work on the subject has been published, but, on the other hand, there is a great lack of agreement about the methods of measurement to be adopted and the interpretation of the results. The authors have endeavoured to give accurate descriptions of the experimental work which has been done upon the viscosity of pure liquids, mixtures, electrolytic solutions, and colloids, and the

monograph contains excellent chapters upon the connection between viscosity and chemical constitution, and the application of the results obtained to the investigation of some problems in organic chemistry, such as the determination of the configuration of the acetaldehyde phenylhydrazones, is described.

The Principles of Inorganic Chemistry. By WILHELM OSTWALD. Translated with the Author's Sanction by ALEXANDER FINDLAY, M.A., Ph.D., D.Sc. Fourth Edition. London: Macmillan and Co., Ltd. 1914.

IN the third German edition from which this English translation has been prepared the early chapters were considerably altered, and additions were made which greatly increased the value of the book as a comprehensive treatise on pure inorganic chemistry. Thus a new chapter was provided on solutions, which treated of the properties and general laws of solutions and the application of these laws in the separation of mixtures, and the phenomena of changes of physical state and the general properties of mixtures were discussed. The chapter on radio-active substances have been revised and enlarged by the translator, and gives an excellent *résumé* of the subject.

An Elementary Treatise on the Calculus for Engineering Students. By JOHN GRAHAM, B.A., B.E. Fourth Edition. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1914.

THE author of this very useful book has a thorough knowledge of the requirements of engineering students and of the difficulties which beginners meet with in the study of the calculus. Throughout the book the application of the principles of the calculus to practical problems is kept in view, and some very interesting typical examples are worked out in full, while the large collection of unworked problems to which only the answers are given will afford the student ample practice. An introduction has been added to the fourth edition, giving a brief outline of the more advanced parts of Algebra and Trigonometry, with which the student should be familiar before he begins to use the book, and also enumerating some results and formulæ of co-ordinate geometry.

Baumé and Specific Gravity Tables. By NAT. H. FREEMAN. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1914.

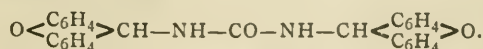
THIS book of specific gravity tables for liquids lighter than water is particularly well printed and will be found convenient in use. The specific gravities are given to seven figures, and to save the user of the book trouble the difference, and also the difference of the differences, are tabulated.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 51, April 14, 1914.

Gravimetric Analysis of Urea.—R. Fosse.—Xanthidrol is a valuable reagent for the quantitative analysis of urea, with which it forms a definite crystalline product of formula—



This compound is only very slightly soluble, and its molecular weight is seven times as great as that of urea. By elementary analysis it is easy to control both the

identity and purity of the precipitate. The solution of urea is first treated with 3.5 times its volume of acetic acid and then half its volume of alcoholic xanthidrol is added. After an hour the crystalline precipitate is washed, dried, weighed, and analysed. According to another method 3.5 times the volume of acetic acid is added, then half a volume of solution of xanthidrol in methyl alcohol, introduced at intervals of ten minutes. The crystals are collected one hour after the last addition.

No. 16, April 20, 1914.

Action of Sodamide upon Allyl Dialkylacetophenones. General Method of Synthesising Trialkylpyrrolidones.—A. Haller and Edouard Bauer.—In order to decompose allyldimethylacetophenone with sodamide one and a quarter times the theoretical quantity of the latter is added to equal volumes of the ketone and benzene. A little water is then added, the liquid is neutralised with acid, saturated with ammonium sulphate, and treated with ether. On evaporation and rectification a product of formula $C_{17}H_{13}ON$ is obtained. It has none of the functional properties of allyldimethyl acetic amide, and from its reactions it is found to be 3,3,5-trimethylpyrrolidone. This result is confirmed by synthesis.

Action of Ammonia and Amines on Carbon Subnitride.—Charles Moreau and Jacques Ch. Bongrand.—Ammonia acts immediately and very violently upon carbon subnitride, the product being amino butene dinitrile, $CN-C(NH_2)=CH-CN$. This substance is hydrolysed by dilute acids, the reaction occurring in three stages. Butenol dinitrile is first formed, and at once isomerises into oxalacetic nitrile. This last compound then splits into hydrocyanic acid and cyanacetic acid. The tertiary amines have no action on carbon subnitride. The primary and secondary amines, on the contrary, act on it violently, the products being similar to those obtained with ammonia. They are hydrolysed by dilute acids regenerating the base, and giving hydrocyanic and cyanacetic acids.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvii., No. 6, 1914.

Formation of Red Phosphorus by Oxidation of Phosphorus Vapour.—V. Köhlschütter and A. Frumkin.—Red phosphorus is obtained by the cautious oxidation of phosphorus vapour at the ordinary temperature. If gaseous oxygen is introduced in very small quantities into the saturated vapour a dark red homogeneous and transparent product is obtained, which is the result of the incomplete oxidation of the phosphorus vapour. When part of the oxygen and phosphorus contained in it is split off it is converted into red phosphorus. Thus the primary red product is analogous to the intermediate products which appear during the transformation of white phosphorus by phosphorus iodide and tribromide, but, in the formation of red phosphorus from these, constituents are split off which again react with the white phosphorus.

Action of Sodium Hydrosulphide on Tellurium and Selenium.—L. Tschugaeff and W. Chlopin.—When sodium hydrosulphide or rongalite (the double compound of hypothetical sodium sulphoxylate with formaldehyde) acts on metallic tellurium or selenium in alkaline solution a crystalline hydrate of sodium telluride or selenide is obtained. By benzylation with benzyl chloride or with dimethyl phenyl benzyl ammonium chloride benzyl telluride, $(C_6H_5CH_2)_2Te$, is obtained.

Bulletin de la Société Chimique de France.
Vol. xv.-xvi., No. 7, 1914.

Catalytic Preparation of New Ketones.—A. Mailhe.—When mixed vapours of the toluic acids and hydrocinnamic are passed over ferric oxide heated to 470–480° good yields of the three tolylhydrocinnamyl ketones are obtained. In the same way a mixture of anisic acid and ordinary acetic acid gives anisylmethyl ketone, and other mixed ketones can be prepared similarly.

MISCELLANEOUS.

The Royal Society.—Vol. xiii. of the Royal Society's Catalogue of Scientific Papers is the first of the fourth series, which will comprise the titles of papers published or read during the period 1884–1900, and will conclude the work undertaken by the Royal Society, namely, a complete collection of the titles of papers for the whole of the 19th century. The present volume, which will shortly be published, covers the letters A and B. Vol. iii., Part II. of the Subject Index, arranged under the superintendence of Dr. Herbert McLeod, Director of the Catalogue, will also be ready immediately. It deals with Electricity and Magnetism and contains 23,300 entries, thus making in all 56,644 entries for the subject Physics for the years 1800 to 1900 inclusive.

The van't Hoff Fund for the Endowment of Investigators in the Field of Pure and Applied Chemistry.—In agreement with the regulations of the van't Hoff Fund, founded on June 28, 1913, persons interested are informed herewith of the following particulars:—The foundation, whose residence is Amsterdam, and of which the supervision is vested in the Royal Academy of Sciences there, gives from the rents of the Fund every year before March 1, and beginning with March 1, 1915, endowments to investigators in the field of pure and applied chemistry who apply for such an endowment before November 1 next to the Committee charged with considering the applications and awarding the grants. At present this Committee is constituted as follows:—A. F. Holleman, President; S. Hoogewerff; A. Smits; F. M. Jaeger, Secretary. If desirable this Committee may appoint still other members for one year only, to co-operate in judging of the applications made. The names of persons to whom a grant is allowed will be published. The grantees are requested to send to the Committee some copies of the papers relating to the results of their work; but for the rest they are at liberty to choose the manner of publication, as well as the journal, in which they like to publish their results, if only they mention the fact that the research was made with an endowment from the van't Hoff Fund. The amount available over 1915 is about £67. Applications should be sent, registered by post, to Het Bestuur der Koninklijke Akademie van Wetenschappen; bestemd voor de Commissie van het van't Hoff-fonds, Trippenhuis, Kloveniersburgwal, te Amsterdam, with a detailed account of the proposed use of the grant, and of the reasons on which the candidates ground their claim.—In the name of the Committee of the van't Hoff Fund, A. F. HOLLEMAN, President; F. M. JAEGER, Secretary.

MEETINGS FOR THE WEEK.

- MONDAY, 8th.—Society of Chemical Industry, 8. "Dickson Centrifuge System of Sewage Treatment," by E. H. Tripp.
"Studies on the Reduction of Uranium Oxide," by E. K. Rideal. "Contribution to the Discussion on Paper, 'Bleaching of Chemical Pulp,' by Baker and Jennison, and 'Bleaching Efficiency considered in Connection with Suggested Standard for Testing Bleaching Qualities of Chemical Wood Pulp,'" by C. Beadle and H. P. Stevens.
- Royal Institution, 5. General Meeting.
- TUESDAY, 9th.—Royal Institution, 3. "Celestial Spectroscopy," by Prof. A. Fowler, F.R.S.
- THURSDAY, 11th.—Royal Institution, 3. "Faraday and the Foundations of Electrical Engineering," by Prof. Silvanus P. Thompson, F.R.S.
- Royal Society, 4.30. (The Croonian Lecture). "Bearing of Cryptological Research on Heredity," by Prof. E. B. Wilson, of Columbia University.
- Biochemical Society, 5.30. (In the Institute of Physiology, University College, London).
- FRIDAY, 12th.—Royal Institution, 9. "Some Aspects of the American Democracy," by Hon. Walter H. Page, LL.D., The American Ambassador.
- SATURDAY, 13th.—Royal Institution, 3. "Studies on Expression in Art," by Sigismund Goetze.

THE CHEMICAL NEWS.

VOL. CIX., No. 2846.

THE PREPARATION OF EYE-PRESERVING GLASS FOR SPECTACLES.*

By Sir WILLIAM CROOKES, O.M., F.R.S.

(Continued from p. 267).

Measurement of Infra-red Radiation.

BEFORE I had tried many experiments with the thermo-pile and black mica another difficulty cropped up. The heat radiated from the Nernst glower gradually warmed up the apparatus, and unless a long time was allowed between each observation I never could get the index ray of light to return to zero. This and the little sensitiveness of the instrument used induced me to try a mercurial thermometer in place of the thermo-pile, all other arrangements being as before. The thermometer was specially constructed with a concave bulb coated with carbon from burning camphor. It was divided into tenths of a degree, the scale being about 9 mm. to a degree.

To test, a selected plate of black mica was permanently fixed in the apparatus between the bulb of the thermometer and the slide containing the glass. First of all, upon lighting the Nernst lamp, the rise in temperature was taken, having only the mica between the lamp and the thermometer. The thermometer was observed from a distance through a cathetometer. It was allowed to rise about 1° C., and then with a stop-watch the further rise in sixty seconds was observed. A mean of four observations in this way gave a rise in sixty seconds of—

$$\left. \begin{array}{l} 1.75 \\ 1.60 \\ 1.725 \\ 1.675 \end{array} \right\} \text{mean } 1.683.$$

In making a determination of diathermancy, glass plates 2 mm. thick were prepared and placed close to the thermometer bulb in a holder having a $\frac{1}{4}$ inch hole; ten observations were made and the mean taken as the value, which was given in percentages of 1.683.

Thus with glass No. 129; mean rise in sixty seconds = 0.26° C.

$$\frac{0.26 \times 100}{1.683} = 15.4^\circ \text{ C.}$$

A mean of ten similar observations gave a value which was taken as the diathermancy of the glass to dark heat. Its athermancy is obtained by subtracting this value from 100. In this way a multitude of glasses were tested, and recently the results have been plotted on a curve which was found to correspond closely with the result subsequently obtained by the radiometer method.

The Radiometer Balance.

In early papers on "Repulsion Resulting from Radiation,"† I showed that the blackened surface of a radiometer was repelled by all the rays of the solar spectrum, from the ultra-violet to a distance at the red end extending far into the ultra red, the maximum intensity being a little distance below the spectrum line A.

An instrument was accordingly made based on the principle of the radiometer, and somewhat resembling the apparatus described in a paper read before the Royal Society in 1875,—"On Repulsion Resulting from

Radiation."‡ It is a torsion balance in which the beam moves in a horizontal plane. Figs. 1 and 2 show the details of the instrument, the latter references being the same in each figure. A B is a thin glass tube, with a bulb at the end, B, and ground flat at the end, A. To the centre of A B is sealed an upright tube, C D, having an arm, E, blown to it for the purpose of attachment to the pump. F G is a very light arm of aluminium carrying at the end, G, a disc of silver-flake mica coated with lamp-black. At the end, F, is a small counterpoise to allow the arm to hang level. H is a glass stopper to the upper part of the tube, C D, which is widened out to form a cup to hold mercury. The stopper in the cup is accurately ground in the tube, as long a surface as practicable being in contact. The horizontal arm is suspended from the stopper by a bifilar suspension of fine quartz fibres, I J, which are attached to the arm F G by an aluminium stirrup holding at its upper end a silvered glass mirror of one metre focus. The vertical tube is blown out and the edges ground flat at the part where the mirror hangs; a flat piece of glass is cemented to it, forming a window through which pass the entering and emerging index beams of light. The end A of the horizontal tube is left open to allow of the adjustment of the arm in its stirrup, and then it is sealed with a flat piece of glass cemented on. The stopper, H, is lubricated with drops of burnt indiarubber so that it can be smoothly rotated to allow the arm to be brought accurately to zero.

Fig. 2 shows the arrangement of the apparatus fitted for testing the samples of glass. The radiometer balance is enclosed in a wooden box having two holes opposite the mirror and the end of the blackened disc at the torsion arm. Great precautions must be taken to avoid all extraneous radiations from acting on the black disc; a slightly conical card tube, as narrow as the angular movement of the ray of light will admit, is attached to the window at K in front of the mirror, S, and another to the bulb at L opposite the black disc.

The heat radiation used in these tests is emitted from a Nernst glower, M, enclosed in a metal box with an open end. In front of the glower is an aluminium screen, N, pierced with a centimetre hole. A shutter, O, can be moved up and down by an arm close to the observer. The shutter screen is made of a piece of cork an inch thick, having on each side a plate of polished aluminium. In this way the heating up of the shutter when it is obscuring the ray from the glower is effectually prevented. At P is a frame for supporting the piece of black mica, and at Q is a sliding carrier holding the piece of glass under examination. This is so arranged that it can be drawn out and another piece of glass put in without causing any jar. Behind the glass is an aluminium screen, R, with a hole in it one centimetre in diameter. The vacuum must be a rather high one, about 40 millionths of an atmosphere.†

The whole apparatus is closely packed with cotton-wool, so that no radiation can get to the black disc but that which comes through the window opposite. The box containing the radiometer balance is firmly attached to the main wall of the house, to avoid as much as possible interference from vibration caused by movements in the room. A spot of light reflected by the mirror, S, from another luminous source is received upon a graduated screen 1 metre distant in the usual manner.

Testing Synthetic Glasses for Diathermancy.

The mode of procedure is thus:—The mica is put in its place and the lamps started. In about ten minutes the zero is adjusted by means of the rotating stopper. When the spot of light is at zero the shutter, O, is raised, and the extent of the deflection noted. At the end of the first half swing the shutter is lowered, and the whole is left at

* Read before the Royal Society, November 13, 1913. From the *Philosophical Transactions of the Royal Society*, Series A, vol. ccxiv., pp. 1—25.

† *Phil. Trans. Roy. Soc.*, 1876, Part II., vol. clxvi., pp. 355—361.

‡ *Roy. Soc. Phil. Trans.*, 1875, vol. clxv., Part II., pp. 533—4—5.

§ *Phil. Trans. Roy. Soc.*, 1876, Part I., p. 301 (The Bakerian Lecture), and *Roy. Soc. Proc.*, vol. xxv., p. 305.

rest until the light is again at zero. The glass under test, T, is now put in its carrier and slid into place, and the extent of deflection of the spot of light noted when the shutter is raised. The amount of deflection with the same piece of mica interposed is thus obtained with many different kinds of glass, and from the data the order of obstruction to heat rays can be calculated for each. It is a necessary precaution to verify the readings once or twice, and to allow the spot of light to come accurately to zero. It is inclined to shift if observations are repeated too rapidly, owing to the retention of heat by the blackened face of the radiometer disc, and the consequent repulsion between it and the front of the bulb B. This effect soon goes off if a little time elapses between the different observations.

The deflection of the spot of light when the dark mica alone is interposed gives the effect of the total heat ray, and the lessened deflection when the glass under test is also interposed is a measure of the heat it cuts off. By dividing the scale divisions traversed by the luminous index when both glass and mica are in the path of the heat ray by the number of scale divisions traversed when the mica alone is interposed, the result gives the amount of heat obstructed.

Addition of Absorbing Media to the Soda Flux.

The first point to be settled is the effect of dissolving various metallic oxides by fusion in the clear colourless glass. The metal is added in the form of oxide, nitrate, or other salt, according to which is easiest to obtain pure. Unless oxidation of other ingredients is to be avoided the nitrate is preferred, as the copious liberation of gas during the fusion stirs up the fused mixture and assists in making it homogeneous in a much shorter time.

To be generally useful, it is desirable to obtain a glass which will absorb rays of longer wave-length than about λ 7200, and so cut off dark heat radiation. It should also be opaque to wave-lengths shorter than about λ 3550, thus cutting off the most chemically active rays, and also those which give rise to ionisation, *i.e.*, cause the air through which they pass to conduct electricity.

Working in a vacuum and with sensitive plates of emulsion containing no gelatine, Dr. Schumann succeeded in photographing ultra-violet rays as short as λ 1000. In a paper recently read before the French Physical Society by MM. Karl Stockhausen and Fritz Schanz, it is stated that the harmful action of light on the eye is due to the ultra-violet rays. It is also shown that the cornea is opaque to rays shorter than λ 3200.

The crystalline lens is opaque to rays shorter than λ 3500, and rays of longer wave-lengths than this reach

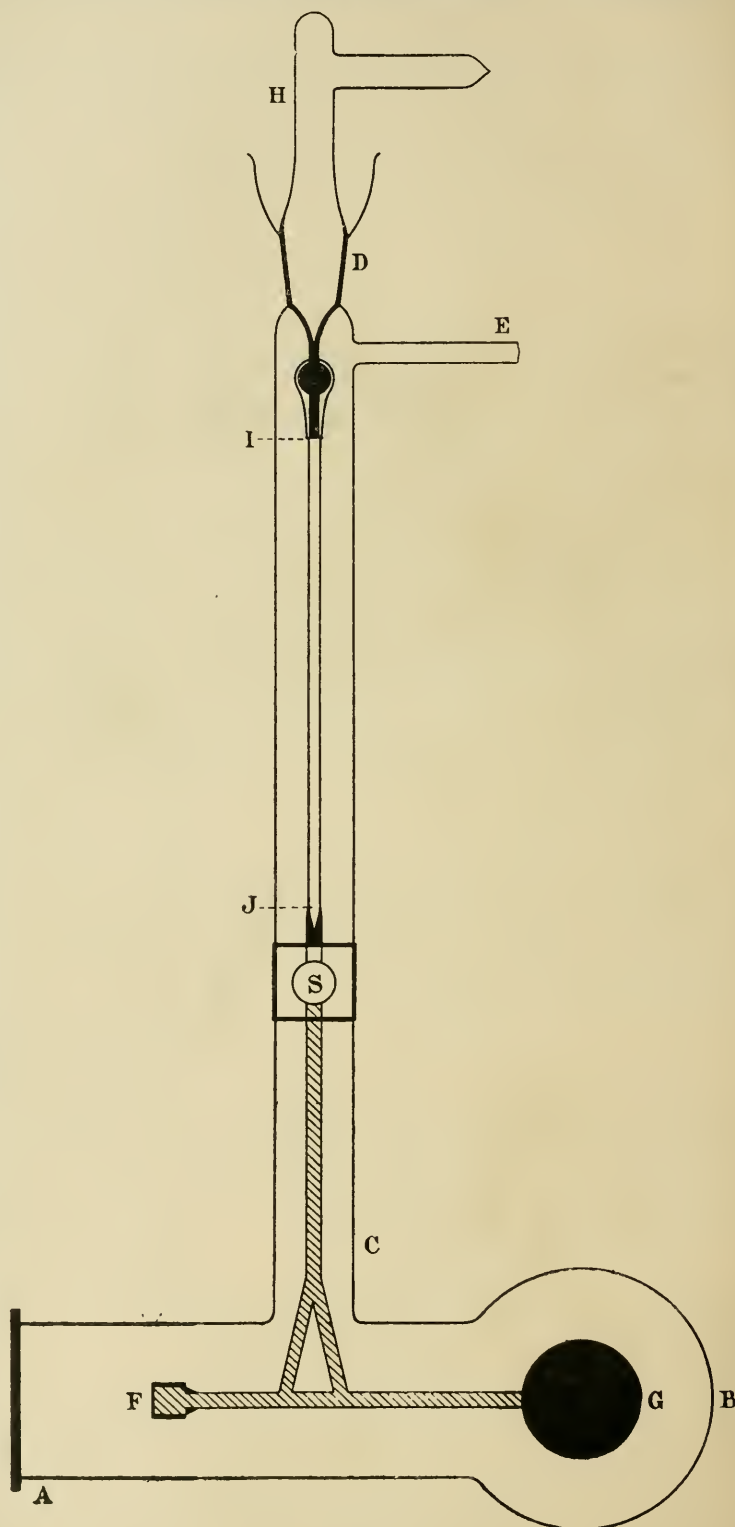


FIG. 1.

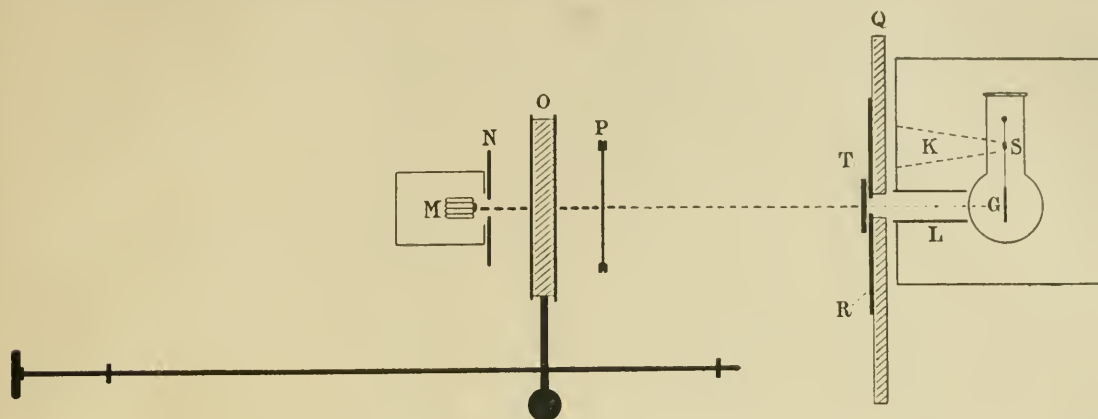


FIG. 2.

- A, B, C, D, E. Case of radiometer (Fig. 1).
F, G. Radiometer arm with blackened mica disc.
H. Ground glass joint (Fig. 1).
I, J. Quartz fibres (Fig. 1).
K. Guard tube in front of mirror S.
L. Guard tube in front of radiometer disc.
M. Nernst glower.

- N. Aluminium screen.
O. Shutter.
P. Black mica screen.
Q. Carrier for holding glass specimen.
R. Aluminium screen.
S. Concave mirror, one metre focus.
T. Glass specimen under examination.

the retina. As the transparency of ordinary spectacle glasses is limited to λ 3000, it follows that a considerable amount of ultra-violet radiation may reach the cornea through ordinary spectacles.

Method of Testing Glass.

Single metals were at first tried in varying quantities to see if from the colour and properties communicated to the glass they were worth further examination. Each specimen is cut and polished into a plate 2 mm. thick. The plate so prepared is first tested in the spectrum apparatus to ascertain the upper limit of transmission of the ultra-violet rays. It is next put into the radiometer balance to see the percentage of heat cut off, then tested in Chapman Jones's opacity balance* to see the percentage of luminous rays transmitted, and finally the colour is registered in a Lovibond's tintometer.†

A large proportion of the known metallic elements were tested in this manner, and a considerable number were proved to be unsuitable. After experiments extending over several months the following elements were selected as likely to be worthy of further experimentation by combining the metals two, three, or four at a time in one glass so as to enable the advantages of one to make up for the shortcomings in another.

Cerium.	Manganese.
Chromium.	Neodymium.
Cobalt.	Nickel.
Copper.	Praseodymium.
Iron.	Uranium.
Lead.	

I will now take the metals selected for further trials, and give the results of the preliminary test of the glasses so as to ascertain their behaviour in the four instruments above described.

Cerium.

One of the most important additions to soda flux is ceria, which gives a practically colourless glass. Cerium

nitrate was generally used, and occasionally cerium borate and ceric oxide. Trial glasses were made, the proportion of metal varying from 1 per cent to 7.5 per cent. The conclusion arrived at on tabulating and considering the results shown by this series of glasses, is that cerium is of value in cutting off the ultra-violet rays. The glasses are very slightly coloured, and allow nearly all the luminous rays to pass. The heat absorption is about 30 per cent, and does not vary much with the amount of cerium present.

Chromium.

This metal, in quantities of less than 1 per cent in the glass, exerts a strong action on the ultra-violet rays, cutting them off down to the blue (λ 4550). In larger proportions, either singly or mixed with other metals, the absorption extends as far as λ 5600 (about the middle of the green). Its heat obstructing power is not on a par with that of uranium, being about 30 per cent for 1 per cent of chromium metal. The luminous rays transmitted by chromium glass containing 0.85 per cent of metal are 37 per cent of the total light, the colour of the glass being green.

Cobalt and Nickel.

Cobalt colours glass a rich blue, and then transmits ultra-violet rays of shorter wave-length than about λ 3200. It cuts off 40 per cent of the heat, and unless in very small quantity obstructs too much light to be of use. Nickel colours glass brown. In glass its absorption of ultra-violet light is about the same as cobalt. It obstructs a little more heat and is more transparent to light. These two metals separately are of no use for the present purpose, but united they have the valuable property of neutralising each other's colour and giving the glass a neutral grey tint.

It is noteworthy that the colours of nickel and cobalt in aqueous solution are green and pink, whilst in solid solution in glass they are brown and blue, in each case complementary to one another.

Solutions of nickel and cobalt sulphates, containing 5 grms. to 100 cc. of water, mixed together in the proportion of 2.5 cc. Ni to 1 cc. of Co, gave a mixture of a neutral grey colour. The mixture was divided into two parts; one was gradually heated to the boiling-point, while the other was left for comparison at the temperature of the laboratory (16° C.). Compared with the cold

* "An Opacity Balance," by Chapman Jones (*The Photographic Journal*, vol. xxiii., p. 99).

† The tintometer is an instrument devised by Mr. Lovibond (Messrs. Gallenkamp and Co.). Any colour can be matched by a combination of three sets of glasses, coloured respectively red, yellow, and blue, and numbered in order; the depth of colour increasing with the magnitude of the numbers.

solution, the one at the boiling-point was decidedly pink, and it required a further addition of nickel solution to restore the neutrality of colour at the boiling-point, raising the proportion of nickel to cobalt 3.5 to 1 at 100° against 2.5 to 1 at 16°. As the hot solution cooled the neutral tint gradually changed until it became decidedly green.

The same mixed solution, neutral tinted in the cold, was acidulated with sulphuric acid. It immediately assumed a very faint tinge of pink, but not so decided a tint as the same neutral coloured solution took when heated to the boiling-point.

A solution was prepared containing nickel and cobalt in the proportion of 2.5 to 1; it was evaporated to dryness and ignited. The mixed oxides were then added to the hard soda flux, and the whole melted together at a high temperature; the glass resulting was cut and polished into a plate 2 mm. thick. It was decidedly blue, although the metals were in the proportion to give neutrality at the ordinary temperature when in aqueous solution. More nickel was added in small proportions at a time, and it was not until the proportion in the glass was 1 cobalt to 5 nickel that a neutral grey glass was obtained.

As a colouring agent cobalt is stronger than nickel. It is not easy to get an exact proportion, as the neutral point is difficult to hit with accuracy. If 4 of nickel instead of 5 are used with 1 of cobalt the glass is of a decided bluish tint, while if 6 of nickel are added the colour is brown.

(To be continued).

THE INFLUENCE OF THE ADDITION OF HEDYCHIUM PULP TO CHEMICAL AND MECHANICAL WOOD PULPS UPON THE PHYSICAL QUALITIES OF PAPER PRODUCED THEREFROM.

By CLAYTON BEADLE and HENRY P. STEVENS.

HITHERTO, in the various published investigations on the subject of *Hedychium coronarium*, the results recorded have to do with papers of various kinds, qualities, and substances made from the fibre alone or, in some few instances, with the addition of clay. No results have been published with a view to ascertaining the effects of using *Hedychium coronarium* in admixture with other paper-making fibres. In a paper mill where a commercial trial was made of *Hedychium coronarium* paper of the strong Manila quality, it was decided, subsequent to the production of the Manila paper, to mix some of the beaten *Hedychium coronarium* pulp with long-fibred sulphite pulp. This gave rise to a very strong paper possessing qualities somewhere intermediate between those of strong sulphite and strong Manila. As Hedychium has the property of self-sizing pulp, we thought it would be as well to ascertain whether it imparts these self-sizing qualities to other fibres when used in admixture with them. Also, whether, on the addition of considerable quantities of clay, the paper still retained its sizing qualities.

Certain physical qualities of clay loaded Hedychium papers have recently been dealt with ("The Effects of Mineral Loading upon the Physical Qualities of 'Hedychium' Paper," *Journ. Soc. Dyers and Colourists*, March, 1914, xxx., No. 3), at considerable length. Clay loaded Hedychium papers of the percentage compositions given in Table A were examined to ascertain how far they remained inkproof. It is well known that all ordinary fibres, in order to render them inkproof, have to be sized with rosin (or gelatin), and that the addition of clay calls for an increased consumption of rosin in proportion to the amount of clay retained, that is if the loaded papers are to retain as great an inkproof quality as that of the unloaded.

No.	Date.	Hedychium.	Clay
1.	December 16, 1913..	100.0	0.0
2.	"	91.5	8.5
3.	"	85.0	15.0
4.	"	82.7	17.3
5.	"	73.2	26.8
6.	"	68.6	31.2
7.	"	57.7	42.3

No. 1, consisting of Hedychium and containing no loading, behaves towards ink very much like a strong Manila paper, that is, a broad ink mark showed the liability of repelling the ink on the surface somewhat. The same liability is to be noticed with some very hard tub sized papers. This is a general indication of hard sizing.

No. 2, which contains 8.5 per cent of clay, behaves very similarly, but repels the ink on surface in a somewhat less degree.

No. 3 also, although in the case of 3 the ink spreads in a more normal fashion.

All these are very resistant to ink penetration.

No. 4, containing 17 per cent of clay, shows great resistance to penetration of ink, but the ink spreads on the surface in a uniform manner more like that of a normal paper, and the same may be said of Nos. 5 and 6.

No. 7, which contains 42 per cent of loading, which is an exceedingly high percentage, and with ordinary paper stock would require a large amount of rosin in order to render it properly inkproof, does not show the least penetration to the other side for ordinary substances, and, when Stephens' blue-black ink is used, which we use as a standard, shows practically uniform spreading on the surface and no appearance whatever of penetration to the other side for normal thicknesses.

Composition.		Bursting strain in lbs. per square inch.	
Hedychium.	Mechanical A or chemical B.	A.	B.
Per cent.	Per cent.		
100	0	64.5	58.3
90	10	65.0	67.0
80	20	63.0	63.0
70	30	65.0	60.3
60	40	60.1	68.3
50	50	55.0	70.0
40	60	50.0	66.1
30	70	44.0	61.6
20	80	38.6	58.1
10	90	31.0	61.4
—	100	29.0	54.6

These results, therefore, show that the influence of the parenchyma cells of the Hedychium is so great as to enable papers to be loaded with clay up to the extent of 40 per cent without breaking down the self-sizing qualities. This is in itself a valuable property. It must not furthermore be lost sight of that with most paper-making fibres it would be practically impossible to retain such a large percentage of clay, even with the aid of rosin sizing.

Mixtures of Hedychium pulp and mechanical wood pulp were made of compositions as per Table B. Similar mixtures were made of Hedychium pulp and chemical wood pulp. Papers were made from each of them and carefully tested by ink tests. Papers prepared from the Hedychium mechanical mixtures were also tested by ink tests. Down to mixtures containing 60 per cent Hedychium and 40 per cent mechanical wood, there was no appearance whatever of penetration or spreading upon the surface. In fact such mixtures appear to behave, as regards ink bearing and ink spreading, in the same manner as 100 per cent Hedychium. At 50 per cent Hedychium and 50 per cent mechanical wood there is a slight disposition to spreading laterally, i.e., at right angles to the ink mark, in feathers upon the surface but with practically no penetration. At 40 per cent Hedychium and 60 per cent mechanical wood the

feathery spread on the surface is augmented. At 30 per cent Hedychium and 70 per cent mechanical wood the ink penetration to the other surface is distinctly marked, and both the feathering and the penetration increase with increased quantities of mechanical; thus 80 per cent mechanical more so than 70, and 90 per cent more so than 80 per cent, and, of course, 100 per cent mechanical is quite soft and liable to immediate penetration.

Taking the case of Hedychium-chemical wood pulp mixtures when tested in a similar manner to the above show very surprising results. All of them show no spreading and no penetration. The breaking down in ink bearing qualities is between the paper showing 10 per cent Hedychium and 90 per cent chemical wood, and the 100 per cent chemical wood paper.

It is evident, therefore, that not only has Hedychium when in admixture with clay, mechanical and chemical wood, marked strength-giving and such like qualities, but it acts as a sizing agent as well as a mineral retainer, and the proportion necessary to produce self-sizing will depend not only upon the proportions (percentage compositions) of Hedychium with these other substances, but upon the nature of the substances with which it is mixed. Thus with chemical wood-pulp, a small amount of Hedychium only, such as 10 per cent, is sufficient to produce self-sizing; with mechanical it is at least 50 per cent, and perhaps somewhere about the same proportion with clay.

Table B is also intended to show the influence of admixture of Hedychium with (a) mechanical or (b) chemical wood pulp upon the bursting strain of the papers produced. The first two columns indicate the compositions, the third column relates to (a) mechanical, and the fourth to (b) chemical. The bursting strain is expressed in lbs. per square inch and, for purposes of comparison, is reduced to a standard substance. Each result given in the table is a mean of ten tests. Attempts are always made in such trials to arrive at a uniform substance so as to avoid any further calculations, but where they differ from uniform substances they are calculated to a uniform substance.

Tests were also made (not given in table) of the breaking length of these papers. The results as regards breaking length do not indicate anything particularly striking.

Hedychium for these purposes is beaten fairly short in order to make it operate more as an agglutinating agent than as a fibrous material, and, in each case of that used in admixture with chemical wood, it was so beaten that the bursting strain of 100 per cent Hedychium was made to correspond as nearly as possible with the bursting strain of 100 per cent chemical. Taking the case of the bursting strain of the Hedychium-mechanical mixtures, it will be noticed that the 100 per cent Hedychium has more than doubled the bursting strain of the 100 per cent mechanical. From the results of the top members of the series, there is no evidence of diminution in the bursting strain until the composition arrives at somewhere between 70 per cent and 60 per cent Hedychium and 30 per cent to 40 per cent mechanical. After this point as the percentage of mechanical increases so the bursting strain diminishes.

Hedychium is a pulp which stands the admixture of a certain proportion of other material much inferior to itself without showing deterioration, at least so far as bursting strain is concerned. This is borne out in the Hedychium-mechanical mixtures; it has been observed in cases of admixture with clay, and it is also borne out when one comes to look at the figures obtained with admixtures of Hedychium and chemical wood pulp in which the unmixed chemical wood is only slightly inferior to the unmixed Hedychium. Here it will be observed that, from 100 per cent Hedychium up to 50 per cent Hedychium and 50 per cent chemical, there is a distinct rise in bursting strain, 100 per cent Hedychium being 58 and the 50 per cent being 70, after which there is a distinct fall. We can only account for these results by assuming that there is in the normal Hedychium pulp a surplus of parenchyma cells, that is, more than is required for giving to the Hedychium fibres proper their necessary strength and self-sizing quali-

ties, so that on the addition thereto of any foreign fibre a mixture may be obtained which possesses greater strength or greater bursting strain than the strength-giving constituent, namely, the Hedychium. This is a distinctly valuable property, especially in cases where it is desired to blend Hedychium with other paper-making fibres. Not only is this property to be noted so far as the bursting strain is concerned, but also the breaking length. Thus the mean breaking length of the unmixed Hedychium and chemical, that is, when each unmixed paper is tested and the mean taken for both, is 4.5 kilometres. One would assume in the ordinary course of events that all mixtures of the two would fall somewhere between the figure obtained for the unmixed Hedychium and that obtained for the unmixed mechanical. As a matter of fact, the unmixed Hedychium shows 4.0 kilometres breaking strain, and that containing 80 per cent Hedychium and 20 per cent chemical is 6.0 kilometres. Therefore much stronger paper is obtained by mixing the two than from either of the constituents separately. We wish, however, to point out that far stronger papers are obtainable alone than any of those recorded above when the material is *suitably beaten for the purpose*, i.e., when Hedychium is beaten for long and hairy papers or krafts. Thus the greatest strength so far obtained is somewhere between 10 and 11 kilometres. The Hedychium pulp here used is prepared in such a way as to act as an agglutinating, compacting, and self-sizing agent, and as a mineral retainer. At the same time in some respects it possesses qualities which are quite equal to those of the strong krafts. When, however, the Hedychium and chemical pulps are blended with large proportions of chemical, as, say, equal weights of each, although the bursting strain is very high, the breaking length found is almost exactly that calculated, the observed being 4.77 kilometres and the calculated 4.5 kilometres.

When a fibre is investigated for the first time it is desirable to examine the qualities of paper producible from it without admixture with other fibres, but inasmuch as the qualities of mixtures cannot be inferred and the paper maker works mostly with blended fibres, it is important as a further step to test the qualities of various mixtures. This communication is for the purpose of recording the influence of such mixtures.

THE ESTIMATION OF CARBON DIOXIDE IN THE AIR.—A SIMPLE AND EXPEDITIOUS METHOD.*

By W. M. DOHERTY, F.I.C., F.C.S., Government Laboratory, Sydney, New South Wales.

THE rapid estimation of carbon dioxide in the air of rooms, public halls, factories, or wherever numbers of persons congregate in confined spaces, is sometimes very desirable. The older methods in use are comparatively slow, and in some cases cumbersome. The process I now propose to use, though not perhaps as absolutely accurate as more lengthy methods, is quite near enough for all practical purposes of the hygienist. It is extremely simple, and may be carried out well within the hour from obtaining samples, and in as small a quantity as 100 cc. It is as follows:—

A series of 100 cc. flasks (say, ten in number), well stoppered and filled with water free from carbon dioxide, &c. (preferably distilled water), are emptied at the place where the sample is required to be taken. The stoppers are inserted and the samples taken to the laboratory or tested on the spot. Into each 100 cc. flask a standard solution of sodium carbonate coloured with phenolphthalein is rapidly run, in arithmetically progressive quantities until a limit is reached beyond which it is unnecessary to go.

* "Report of the Australasian Association for the Advancement of Science, Section B (Melbourne Meeting)," vol. xiv.

For instance, in the first flask 4 cc. are placed; in the second, 5 cc.; in the third, 6 cc.; and so on. Two or three flasks should be reserved for final adjustment if necessary. The standard solution of sodium carbonate is of such a strength that each cc. is equivalent to 0.01 cc. of carbon dioxide. (As the air contains normally about 0.04 per cent of CO_2 it will be seen at once why I begin with 4 cc. of the standard solution). The only factor in the process which requires special care is the making up of the standard solution. The calculation and equation used in doing this are here given:—

$$1 \text{ cc. of } \text{CO}_2 \frac{44}{22320} = 0.001971 \text{ gm.}$$

and according to the equation



1 cc. of CO_2 converts $\frac{0.001971 \times 106}{44} = 0.004748$ gm. of Na_2CO_3 into NaHCO_3 .

Thus a solution is made by dissolving 0.4748 gm. of sodium carbonate in 100 cc. of water, a $\frac{1}{4}$ gm. of phenolphthalein being added as the indicator. This solution is carefully adjusted to its proper strength by titration with N/10 acid in the usual manner. If properly made 1 cc. will equal 1 cc. of carbon dioxide (N.T.P.). It can be kept for months unimpaired. The working solution is made by diluting this 100 times with distilled water free from CO_2 , say, 10 cc. to a litre. A standard solution is thus obtained, 1 cc. of which is equivalent to 0.01 cc. of CO_2 . The 100 cc. flasks containing the air to be tested and the standard solution are well and continuously shaken for twenty minutes. The amount of CO_2 expressed in percentage by volume is readily indicated by the number of cc. of standard solution decolorised. This lies between the last decolorised flask and the next in the series which retains its pinkness. A reserved 100 cc. sample can finally be tested with half a cc. more standard solution than was required by the decolorised flask. A correction for actual volume in the 100 cc. flask is made, subtracting, of course, the volume of standard solution added.

It remains but to add that ordinary care will have to be exercised in protecting the standard solution from the natural action of the air surrounding it. This can be done in the burette by the aid of a soda-lime filter, the burette being preferably large enough for the whole set of experiments. The solution may also be conveniently kept in an ordinary separator similarly protected. I do not find, however, that using reasonable expedition in pouring the solution into the burette and in running it into the flasks there is any appreciable alteration in its strength.

AN IMPROVED WATER PUMP.

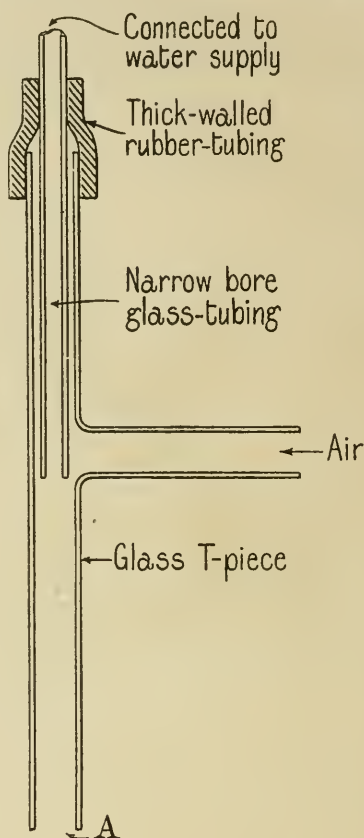
By K. EVANS.

It often happens in a laboratory that a water pump is not always at hand, the available ones being in use or fixed to the water supply at a distance from the apparatus where it is required. The pump described may be of some use in such a case, and may be put together in a few minutes.

A piece of narrow bore glass tubing is inserted in the long arm of a T-tube (glass), the end projecting about $\frac{1}{4}$ in. beyond the junction of the short arm of the T-tube. The inner tube is fixed into the T-tube by means of a piece of thick rubber pressure tubing, the outer end of the tube being attached to the water supply by means of pressure tubing.

A pump so fitted was capable of a suction of 20—30 cubic feet per hour when attached to the ordinary water supply.

The pump can be used to produce a gentle suction, by



substituting for the water supply of the mains, a flow of water from a suitable vessel such as a constant level tank. In this case a long piece of glass tubing is attached to the T-piece at A to act as a fall-tube.

Tanycoed, Carnarvon.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

FORECASTS OF THE WEATHER.

It is generally said that meteorology is an uncertain science. It progresses slowly. However during the last few years meteorology has made some precious discoveries. Among these discoveries we must include the new method of foretelling the weather imagined by a meteorologist of Caen, M. Gabriel Guilbert. This method, founded on the observation of the wind both in its direction relative to the cyclonic and anticyclonic centres, as well as in its speed relative to the barometric gradient, may be summed up in the two following propositions:—(1) The variation of pressure is determined twenty-four hours in advance by the direction and the actual speed of the surface wind; (2) the formation of cyclones and their destruction are connected in all seasons only to the surface wind, to the exclusion of upper currents and naturally to mountain winds. In a paper presented to the Academy of Sciences by Prof. Violle, M. Gabriel Guilbert indicates the results of a long series of forecasts made from October 1, 1912, to May 1, 1914. These previsions, numbering 9000, contain indications as to the rise of the barometer and the future of depressions, sometimes even the designa-

tion of the points or limited regions on which was to take place the next day, the maximum barometric rise or fall, and the approximative numerical value of this maximum. The forecasts relating to the variations of pressure have been realised in the proportion of 86 per cent. Those concerning the future of cyclones have had 89 per cent of successes. And the discussion on the non-successes shows that those really due to the rules of the method do not exceed 2 or 3 per cent. The method then would be verified theoretically from 95 to 98 times per 100.

MARINE CHETOGNATES.

Chetognates are worms, but exclusively marine and pelagic worms. On the outside they resemble a small rigid and transparent war torpedo boat. They swim quickly and straight ahead. M. Joubin, Professor at the Natural History Museum, has just studied them in a paper presented before the Academy by the Prince of Monaco. Several thousands of chetognates were captured during the oceanographic cruises of the Prince. They usually live at a depth varying from 1200 to 4000 metres. The species that live in the mean depths come to the surface at night. A curious fact is that the teeth and hooks of these worms become stronger as the depths at which they live is greater. This is because the marine vegetation becomes poorer in the greater depths; the detritus does not descend into the depths of the abyss. The animals are obliged to live on each other; the strongest devour the weaker; the strongest armed triumph. This is why the chetognates that live at a depth of 4000 metres are more powerfully armed than those that live nearer the surface.

THE 26TH SCIENTIFIC CAMPAIGN OF THE PRINCE OF MONACO.

From July 22 to October 10, 1913, the oceanographic cruise commanded by the Prince of Monaco pursued the course of its operations between the coasts of Europe and those of North America. The oceanographers of the *Hirondelle* wished especially to determine precisely certain observations that they had made the previous year concerning a whole series of animals inhabiting depths below 1000 metres and which are to be found, but only during the night, at 200 metres from the surface. The importance of such a fact is considerable from a physiological point of view, for it allows us to catch a glimpse, or at least to suppose, in these animals an extraordinary facility to undergo, twice in twenty-four hours, the enormous decompression of an ascent equivalent to one or several hundreds of atmospheres, and immediately afterwards the recompression to the same atmospheres. This fact also throws a new light on the existence of the fauna that, in spite of the smallness of its individual members, executes every night, and by the simple means of swimming, followed by a vertical fall or drop, this ascension of one or several kilometres. The great progress realised by the campaign of 1913 consists in the regulating and the employment of a very precious instrument constructed by Schäffer and Budenberg, of Magdeburg, to obtain, by a very precise registration, the curve of the depths visited by the net to which it had been joined. The comparison of the lengths of cable let out, and the speeds of the drawing, with the hours and the depths registered, enables the establishment of a law to regulate the work of the net at the depth that is required, in spite of the complications of such an undertaking. But certain difficulties of details still remain, and these will doubtless be overcome during the next campaign; and then we shall be able to know with an absolute precision the level inhabited or passed through, at the different hours of the day and of the night, by these animals that are so marvellously constructed. But it will still remain to be known why they thus make this regular displacement. It was the Naval Lieutenant Bourée who directed this part of the work. M. Albert Ranc, assistant at the laboratories of the Sorbonne, continued, during this cruise, the researches on the physiology of

fishes, previously begun by him on board the *Hirondelle*, and concerning the presence of sugar in the blood of marine animals. Many other studies interesting to oceanography were pursued as usual, but those quoted above held the first place. We can, at present, remark a certain decrease in the number of operations executed during the oceanographic campaigns of the Prince of Monaco. This is owing to the fact that about 5000 stations having already been made on the Northern Atlantic during the twenty-nine years that these cruises have been prosecuted, a very advanced knowledge in this domain is already acquired. Henceforth it is necessary to cover wider spaces or to give greater amplitude to certain operations in order to complete certain work or to fill up gaps or desiderata.

THE SEARCHING FOR SMALL PLANETS.

M. Louis Fabry, astronomer at the Observatory of Marseilles, proposes two methods to find little planets at each new opposition. In one method, he determines an elliptic orbit by four observations, two of which are made in the preceding opposition, the two others in that which has preceded it. In the other method he utilised four observations in four different oppositions; in this case he calculates summarily the perturbations produced on the planet by Jupiter by considering the orbit of the planet as circular. The second method has been applied by M. Fabry to the planet 308 Polix, the first by M. Henri Blondel, of Marseilles, to the planet 89 Julia. The two planets were found in the places foreseen or nearabouts at a distance of, say, one or two minutes of an arc.

A NEW COMET.

M. Chofardet, astronomer of the Observatory of Besançon, from May 19 to 22 made four observations of the new comet Zlatinsky. On May 19 it was estimated to be of the fifth magnitude, with a brilliant round head, of four minutes in diameter, with a strong central condensation of from four to five seconds thick. A not very luminous tail, thin and rectilinear, stretched as far as one degree from the head at an angle of 17° to the neighbouring pole.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 21, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President,
in the Chair.

THE PRESIDENT announced that in connection with the van't Hoff Memorial a Fund has been established for the endowment of research in the field of Pure and Applied Chemistry. The amount available during 1915 for purposes of research is about £67.

A Committee consisting of Prof. A. F. Holleman (President), Prof. S. Hoogewerff, Prof. A. Smits, and Prof. F. M. Jaeger (Secretary), has been appointed to award grants. Applications for grants should be sent before November 1, 1914, by registered post to "Het Bestuur der Koninklijke Akademie van Wetenschappen; bestemd voor de Commissie van het 'van't Hoff fonds' Trippenhuis, Kloveniersburgwal, te Amsterdam," and applicants are requested to submit a detailed account of the manner in which they propose to spend the grant.

Papers embodying the results of the Research may be published in any journal, but acknowledgment must be made of the source of the grant. Copies of the papers embodying the results of the Research must be forwarded to the Committee.

Messrs. L. J. Hudlestone, A. U. Newton, B. N.

Ghosh, T. E. Hodges, G. P. Furneaux, A. Coulthard, A. Baxter, R. O. Bishop, and S. M. Bosworth were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Frederick George Henderson, 44, Dene View, Wallsend-on-Tyne; Victor Henri, 8, Rue du Puits de l'Ermite, Paris; Robert Ernest Machin, B.Sc., 5, Redcliffe Road, South Kensington, S.W.; Thomas William Thompson, M.A., Queen Elizabeth's Grammar School, Gainsborough.

A Certificate has been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Mr. Probodha Chundra Chattopadhyay, M.A., 90, Manikta Main Road, Harrison Road P.O., Calcutta.

Of the following papers, those marked * were read:—

*141. "Ionisation and the Law of Mass Action. Part III. Utilisation of the Osmotic Data and a New Dilution Law." By WILLIAM ROBERT BOUSFIELD, K.C.

Excellent freezing-point and vapour-pressure data for concentrated solutions of lithium chloride exist, and less complete data for sodium and potassium chlorides, the vapour-pressure data ranging from 40° to 100°. An empirical vapour-pressure formula of the form—

$$h\delta p/p = 2 - Gh - \frac{1}{2} + Ah - 1 - Bh - \frac{1}{2}$$

is found, which gives expression to the data obtained by extrapolation to 18°.

A new dilution law is proposed of the form—

$$\frac{\alpha^2}{1 - \alpha} = K(h - n)\frac{1}{2}.$$

By using this in conjunction with the osmotic relations—

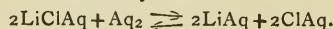
$$\frac{P}{R'T} = \frac{\Delta}{F'} = \frac{\delta p}{p} = \frac{1 + \alpha}{h - n},$$

it is possible to evaluate both α and n .

The values of α and n independently obtained from the freezing-point and vapour-pressure data are found to be in good accord, and give values for n at infinite dilution which are in fair accord with those derived from conductivities.

With the more complete series of data for lithium chloride, it is found that a relation exists between α and n which is independent of temperature in the range considered, namely, $n = 38\alpha - 14$.

This enable the conditions of a saturated solution of lithium chloride at 18° to be examined, which shows that the ionisation reaction may be taken to be—



This gives, according to the law of mass action, the relation—

$$\frac{\alpha^2}{(1 - \alpha)^2} = K' \frac{\beta}{2} (h - n).$$

where β is the weight fraction of the free water, $h - n$, which exists in the form Aq_2 , or dihydrol.

This is identical with the assumed dilution law,—

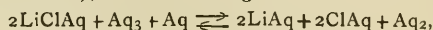
$$\frac{\alpha^2}{1 - \alpha} = K(h - n)\frac{1}{2},$$

if—

$$K = \sqrt{K'\beta/2}.$$

It is shown by reference to the figures for α , n , and β that the relation holds, and that K' has the same value both at infinite dilution and in saturated solutions of lithium chloride.

Alternatively, the reaction might be taken to be—

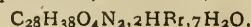


which leads also to the form of the dilution law.

*142. "The Alkaloids of *Ipecacuanha*." By FRANCIS HOWARD CARR and FRANK LEE PYMAN.

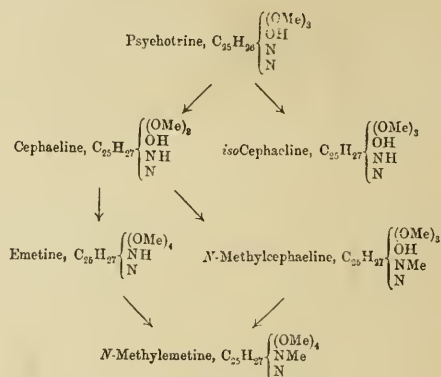
A detailed description was given of an investigation of which a part has previously been reported in a preliminary

note (*Proc.*, 1913, xxix., 226). The salts of emetine, cephaeline, and psychotrine have been fully characterised. *Emetine sulphate*, $\text{C}_{29}\text{H}_{40}\text{O}_4\text{N}_2 \cdot \text{H}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, m. p. 205–245° (corr.); *cephaeline hydrobromide*,—



m. p. 266–293° (corr.); *psychotrine nitrate*, $\text{C}_{28}\text{H}_{36}\text{O}_4\text{N}_2 \cdot 2\text{HNO}_3 \cdot \text{H}_2\text{O}$, m. p. 184–187° (corr.); *psychotrine sulphate*, $\text{C}_{28}\text{H}_{36}\text{O}_4\text{N}_2 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, m. p. 214–217° (corr.); and *psychotrine hydriodide*, $\text{C}_{28}\text{H}_{36}\text{O}_4\text{N}_2 \cdot 2\text{HI}$, m. p. 222° (corr.), are new crystalline salts.

In correction of the previous statement it was shown that emetine and cephaeline are secondary-tertiary bases. Emetine yields a crystalline *N*-benzoyl derivative, $\text{C}_{29}\text{H}_{39}\text{O}_4\text{N}_2 \cdot \text{COPh}$, m. p. 185–186° (corr.), which is a monacidic tertiary base. Emetine is the *O*-methyl ether of cephaeline. It gives *N*-methylemetine, an amorphous base yielding crystalline salts, on methylation. Cephaeline yields on methylation a mixture of emetine, *N*-methylcephaeline, m. p. 194–195° (corr.), and *N*-methylemetine. Psychotrine has the formula $\text{C}_{28}\text{H}_{36}\text{O}_4\text{N}_{2.4}\text{H}_2\text{O}$, and yields on reduction a mixture of cephaeline and isocephaeline (m. p. 159–160°, corr.). The relation between these alkaloids can be expressed as follows:—



The hydrochlorides obtained by the oxidation of cephaeline with ferric chloride were shown to have the formulæ $\text{C}_{18}\text{H}_{18}\text{O}_3\text{NCl} \cdot \text{HCl}$ and $\text{C}_{20}\text{H}_{27}\text{O}_3\text{NCl}_2 \cdot \text{HCl}$ respectively.

143. "The Viscosity of Sugar Solutions." By HEBER GREEN.

In a recent paper Powell (*Trans.*, 1914, cv., 1) claims that the relation between the viscosity and concentration of sugar solutions can be expressed by the equation $\eta_x = \eta_0 A^x$, where x is the ratio of solute to solvent, and in his discussion of previous work quotes the present author (Green, *Trans.*, 1908, xciii., 2027) as having concluded that the "connection between viscosity and concentration is not accurately expressed, even within the limits of experimental error, by any of the various formulæ that have been suggested."

This is, however, an incomplete quotation, the continuation of the same sentence being to the effect that the best concordance is obtained by the use of an expression of the form $\eta_x = \eta_0 A^v/w$, where v and w are the volumes of the solute and solvent respectively.

It was shown that the form of this expression supported by Powell merely neglects any possible contraction which may occur when the sucrose dissolves in water, and is not that which gives the nearest approach to accuracy.

The discrepancies between the calculated and observed viscosities are, in any case, far beyond the experimental error of the measurements made by the present author more than five years ago, and he sees no reason to alter the conclusion arrived at then.

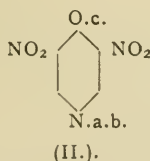
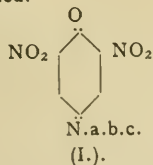
144. "Compounds of Phenanthraquinone with Metallic Salts." By JOSEPH KNOX and HELEN REID INNES.

The following additive compounds of phenanthraquinone and metallic salts have been prepared and analysed: $-C_{14}H_8O_2 \cdot ZnBr_2$, $(C_{14}H_8O_2)_2 \cdot ZnI_2$, $C_{14}H_8O_2 \cdot CdCl_2$, $C_{14}H_8O_2 \cdot CdBr_2$, $C_{14}H_8O_2 \cdot CdI_2$, $(C_{14}H_8O_2)_2 \cdot HgBr_2$.

The relative stability of the zinc and cadmium compounds has been determined by finding the concentration of metallic haloid in aqueous solution with which mixtures of phenanthraquinone and the various double compounds are in equilibrium. This equilibrium concentration is a measure of the relative stability. The lower the equilibrium concentration, the greater is the stability of the compound. It has been found that with a given metal the iodide compound is more stable than the bromide, and the bromide than the chloride, whilst the cadmium compounds are more stable than the corresponding zinc compounds. The stability of the compounds therefore increases with diminishing electro-affinity of both the metal and the halogen. The mercuric compounds are more stable than either the zinc or the cadmium compounds, as is shown by their behaviour towards water, and mercury is the metal of weakest electro-affinity of the sub group. The greater complexity of the mercuric compounds compared with the zinc and cadmium compounds and of the zinc iodide compound compared with the zinc chloride and bromide compounds, also illustrates the increasing tendency to complex-formation with diminishing electro-affinity.

145. "Quinone-ammonium Derivatives. Part III. Dihaloid, Monoazo-, Bisazo-, Nitrotriazol- and Bistriazo-compounds: Attempts to Prepare Derivatives containing an Asymmetric, Quinivalent Nitrogen Atom." By RAPHAEL MELDOLA and WILLIAM FRANCIS HOLLELY.

Taking advantage of the partial and complete reducibility of the nitro-group in 2:6-dinitro-4-trimethyl-ammonium-1-benzoquinone (*Trans.*, 1912, ci., 912; 1913, ciii., 177) the authors have prepared a number of new quinone-ammonium derivatives containing naphtholazo- and triazo groups in place of one or both of the original nitro groups. The constitution of the 2:6-dibromo-derivative (*Trans.*, 1913, ciii., 185) has been proved directly by synthesis from 2:6 dibromo-*p*-aminophenol. Systematic attempts to obtain a quinone-ammonium compound of the type (I.) with three dissimilar radicals attached to the nitrogen atom have led to the discovery that this nitrogen atom appears to be incapable of carrying three different radicals when the weight or size of the latter exceeds some limit at present undetermined. If this limit is exceeded, the alkylation apparently takes a normal course, in spite of steric hindrance, and the isomeric phenolic ether (II.) is obtained.



146. "The Estimation of Carbon Monoxide." By JOSEPH IVON GRAHAM and THOMAS FIELD WINMILL.

As is well known, carbon monoxide is oxidised to carbon dioxide by iodine pentoxide, and various methods of estimating carbon monoxide has been described, based on this reaction. The authors have studied the temperature at which the reaction takes place, and the influence of other gases on its course. A modified form of Haldane's gas-analysis apparatus was described, in which the oxidation may be carried out rapidly, and carbon monoxide estimated with an accuracy of 0.02 per cent.

147. "Alcoholometry and Rational Fractionation." By HENDRIK PIETER BARENDRECHT.

A new distilling apparatus, made from copper, was described, which allows the estimation of alcohol in a

fermented liquid, containing between 2 and 3 per cent of alcohol, by concentrating automatically and in one operation all the alcohol in one twentieth of the original volume. By this arrangement accuracy is easily obtained, even in using an alcoholometer. From very weak solutions, for example, 0.01 per cent, all the alcohol may be distilled off at once in the hundredth-part of a sample of 3 litres.

The construction of this apparatus, as well as of another one (also described), made out of ordinary laboratory glassware, is based on the following principle.

The rectifier, surrounded on the top by an open water-reservoir as a dephlegmator, should have a large volume, filled with a porous substance, to store up and concentrate the volatile liquid, until all of the latter has been boiled out of the sample, and has thereby heated the dephlegmator so far that the liquid can pass to the condenser.

148. "The Resolution of 5-Nitrohydrindene-2-carboxylic Acid." By WILLIAM HOBSON MILLS, HORACE VICTOR PARKER, and ROBERT WILLIAM PROWSE.

With the object of obtaining an optically active benzene derivative in which it should be necessary to take into consideration the relative distribution in space of the substituent groups to account for the optical activity, the authors have prepared 5-nitrohydrindene-2-carboxylic acid, $NO_2 \cdot C_6H_3 < \begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix} > CH \cdot CO_2H$, and have shown that it can be resolved by means of its quinine salt into two antimeric components. Unless the configuration of the nitrophenylene radical is taken into account, the reason for the molecular asymmetry of this compound does not appear. It is evidently due to the asymmetrical disposition of the nitro-group with respect to the two methylene groups, it being in the meta-position to one and in the para-position to the other.

149. "Researches on Pseudo-bases." Part I. "Some Condensation Reactions of Cotarnine, Hydrastinine, and isoquinoline Methyl Hydroxide." By GERTRUDE MAUD ROBINSON and ROBERT ROBINSON.

Cotarnine condenses with 6-nitrohomoveratrole, nitrohomopiperonyl alcohol, or nitropiperonal to yield nitrohomopiperonyl-, nitropiperonylidene-, or nitropiperonyl-hydrocotarnine respectively. The condensation of isoquinoline methyl hydroxide with 6-nitrohomoveratrole, and of hydrastinine with itself, was also described.

150. "Molecular Conductivities of Iodoanilinesulphonic Acids." By MARY BOYLE.

The following moniodoanilinesulphonic acids have been prepared and the conductivities of their aqueous solutions at 25° determined; 2-, 3-, and 4-iodoaniline-6-sulphonic acids, 2-, 3-, and 4-iodoaniline 5-sulphonic acids, and 2- and 3-iodoaniline-4-sulphonic acids. In all cases where iodine is introduced into an orthoposition to the amino-group, a very considerable increase in molecular conductivity occurs; the increase is much less marked in the case of *m*- and *p*-iodo-substituted acids.

151. "The Action of Steam on Sodium Chloride." (Preliminary Note). By SOLOMON ENGLISH and WILLIAM ERNEST STEPHEN TURNER.

Some years ago Emich (*Ber.*, 1907, xl., 1482) described an experiment in which the production of hydrogen chloride from salt and water was demonstrated by dropping water on sodium chloride heated in a platinum crucible. Another and simpler way of demonstrating the reaction is to drop a solution of salt on the surface of a platinum basin at bright red heat, when not only hydrogen chloride can be detected in the issuing vapour but the residue is distinctly alkaline.

The authors have attempted to determine the extent to which this hydrolytic decomposition occurs by passing steam over sodium chloride in a platinum boat heated to varying temperatures. There is no appreciable action at and below 500°, but it becomes recognisable at 700°, and

increases steadily with rise of temperature, measurements having been made up to 1000°. Sodium chloride possesses an appreciable vapour pressure below its melting-point (800°), and the reaction appears to take place mainly between the salt vapour and steam. In porcelain tubes, however, the amount of hydrogen chloride found exceeds the alkali left as residue, and so far the authors have been unable to trace the reason for the discrepancy. They hope to repeat the determinations in a platinum tube.

152. "Experiments on the Synthesis of the Benzoterpenes." Part I. "Derivatives of Benzonor-p-Menthane." By FRANCIS WILLIAM KAY and ALLAN MORTON.

An account was given of the synthesis of some representatives of a new class of terpenes, described as the *benzoterpenes*, which have been obtained from the various derivatives of α -naphthoic acid with the aid of Grignard's reagent.

PHYSICAL SOCIETY.

Ordinary Meeting, May 22, 1914.

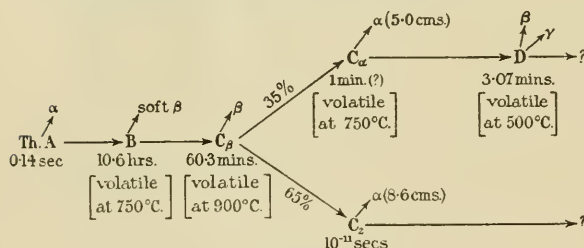
Dr. A. RUSSELL, Vice-President, in the Chair.

A PAPER entitled "Volatility of Thorium Active Deposit," by T. BARRATT, B.Sc., and A. B. WOOD, M.Sc., was read by the former.

On heating thorium active deposit to various accurately measured temperatures up to about 1250° C. it is found that B and C each commence to volatilise at 750° C., but the volatilisation is not complete until 1200° C. is reached, the measurements being made by an α -ray electroscope. The C curve is peculiar, being similar to two of the B curves placed end to end, the inflexion occurring between 750° C. and 900° C., where about 35 per cent of the α -activity is removed.

When measured by β radiation, C is not volatile until a temperature of 900° C. is reached. D commences to volatilise at 500° C.

In explanation of these results it is assumed that the part of C which produces β -rays, viz., C_β , is a separate product, which is not so readily volatile as C_α , and the following scheme of disintegration is suggested:—



DISCUSSION.

Dr. R. S. WILLOWS congratulated the authors on their able treatment of the subject. The suggested scheme met most of the requirements of the case and was not in contradiction with any of the other known properties of the thorium series. He hoped the authors would extend their work to other radio-active series.

Dr. S. RUSS drew attention to the apparent lack of parallelism between the characteristics of the thorium and radium series. The volatility of thorium B appeared to be not very different from that of thorium C, whereas in the radium series, radium B is the most, and radium C the least, volatile of the series. Again, the authors concluded that there was no appreciable difference in the volatility of the thorium active deposit from a quartz or a platinum surface, whereas there was an appreciable difference in the case of the radium active deposit, as Dr. Makower had shown.

Mr. D. OWEN observed that one of the products was stated to have a period of 10^{-11} second. He thought it

hardly possible to catch a product which only lived for that time.

Mr. BARRATT said that only two surfaces were used, quartz and platinum, on account of the high temperature to which they had to be subjected. In these cases there had certainly been no difference. When different acids were used, considerable differences were observed in the temperature of volatilisation. The period, 10^{-11} second, assigned to ThC_2 was simply in order to fit the Geiger-Nuttall relation. The curve connecting log (γ) and log (Range) is a straight line, and the period 10^{-11} second was necessary to make the product fit the curve.

A paper entitled "The Passage of α -Particles through Photographic Films," by H. P. WALMSLEY, M.Sc., and W. MAKOWER, M.A., D.Sc., was read, in the absence of the authors, by Dr. S. RUSS.

It has been shown by Kinoshita that when an α -particle strikes a grain of silver halide, that grain is subsequently capable of photographic development. It therefore seemed probable that the path of an α -particle projected tangentially to a photographic film should, after development, be visible under a microscope. This was shown to be the case, and micro-photographs showing the tracks of α -particles through a photographic plate have been obtained. The effect of "scattering" of α -particles can also be seen in the photographs, and this method may prove of use in studying the scattering of α -particles by heavy atoms such as silver. This method of studying the path of an α -particle possesses the advantage of great simplicity.

A paper "On a Null Method of Testing Vibration Galvanometers" was read by S. BUTTERWORTH, M.Sc.

The methods usually employed in the determination of the constants of a vibration galvanometer involve the measurement of a deflection under three different conditions. Two of these deflections can only be obtained very approximately.

By extending the theory of the vibration galvanometer it is shown how the constants may be determined by methods which involve only the measurement of one deflection. The remaining measurements are carried out on an alternating-current bridge, and the results obtained are practically independent of the wave-form of the source.

The principle of the method depends on the fact that a vibration galvanometer behaves as a parallel combination of a conductance, a capacity and an inductance, in series with a resistance. It is shown how to balance such a combination, and the method is illustrated experimentally. The constants of various galvanometers are quoted in order to show the applicability of the method. Other uses of the bridge are suggested.

DISCUSSION.

Mr. A. CAMPBELL remarked that it was most interesting to find that the electrical behaviour of a circuit capable of dynamical resonance could be imitated exactly by putting in parallel a resistance, a condenser, and an inductance. It was a pity that this combination could not be realised in practice since the inductance must have zero resistance. However, Mr. Butterworth got over the difficulty by his special form of bridge. The limitations of this bridge somewhat lessened the range of application to practical cases, and he hoped that the author would be able to modify the bridge so as to remove these limitations.

Mr. D. OWEN stated that he had found no difficulty in maintaining the frequency of the source sufficiently steady to maintain the voltage sensitivity of a vibration galvanometer constant within 1 or 2 per cent for a considerable time. The author's analysis of the vibrating coil was very ingenious, but one would like to know whether sensitivities calculated by his rather complex bridge agreed with those obtained by the usual direct method.

Dr. R. S. WILLOWS asked whether the method could be used to find the dielectric constant of a slightly conducting liquid; if so, was it sensitive enough to be practically useful and did the largeness of the required inductance again limit its applicability.

Mr. BUTTERWORTH, in reply, stated that the method would apply to any vibrating system provided that the conditions mentioned in the paper could be satisfied. It was true, as Mr. Owen had pointed out, that the voltage sensitivity of certain galvanometers could be determined very precisely. This held in the case of instruments capable of developing a high back E.M.F. The reduction of current at resonance would then prevent any considerable rise in the vibration in spite of the large increase in current sensitivity. The application of the method to the measurement of small capacities required investigation.

"Experiments with an Incandescent Lamp" were described and exhibited by Mr. C. W. S. CRAWLEY and Dr. S. W. J. SMITH.

The first of these experiments was due to Mr. Addenbrooke, who, using a 100-volt lamp filled with paraffin oil (after removing the tip) as a convenient high resistance in a 200-volt circuit, noticed that some of the many bubbles forming on the filament behaved in a curious way. Instead of rising at once to the surface from the point at which they formed they ran down the legs of the filament, against gravity, and then escaped at the leading-in wires.

Dr. Smith, led to repeat this experiment by Mr. Crawley, discovered another, more striking, phenomenon. Placing the 100 volt lamp in a 100-volt circuit in series with a variable resistance (conveniently a water-trough) it was found possible, by momentarily cutting out most of the resistance, to obtain a single bubble upon the wire. The behaviour of such a bubble is very interesting to watch. Instead of escaping at either terminal, as in Mr. Addenbrooke's experiment, it travels backwards and forwards between the two, "looping the loops" of the filament in a fascinating way during every journey.

The peculiarities of this phenomenon, which can be obtained with either direct or alternating supply, have been analysed by examining the size and motion of the bubble under various conditions, and also by using filaments of different materials and liquids of different boiling-points.

It was shown, from the experiments, that a rapid fall of temperature from the wire through the liquid, in the region through which the bubble moves, is an essential condition of the phenomenon, and also, from theoretical considerations, how this condition can be used to explain why the bubble moves in the manner described.

Mr. Crawley pointed out, in connection with the first experiment, that the lamp proved most satisfactory, being able not only to absorb more power than with a vacuum, but also to stand momentary overload much better.

NOTICES OF BOOKS.

Nucleic Acids, their Chemical Properties and Physiological Conduct. By WALTER JONES, Ph.D. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

THIS monograph discusses with great completeness a very important branch of biochemistry, and it will be the more welcome because no treatise devoted exclusively to the subject has appeared before. The author is well qualified to supply the want, having done a considerable amount of valuable original work on the nucleic acids and allied substances, and he displays a sound critical judgment in his estimation of the value of the researches and deductions of other investigators. It is perhaps no disadvantage that his views are generally very definitely expressed, and that he shows no tendency to halt between two opinions. In the first part the chemical properties and the structure of the thymus and yeast nucleic acids are exhaustively studied, and in Part II. their physiological conduct is treated in detail. An appendix describes some practical work, such as the preparation of the nucleic acids and the analytical chemistry of the purine and pyrimidine derivatives.

The Simpler Natural Bases. By GEORGE BARGER, M.A., D.Sc. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

THIS monograph deals with the basic substances found in animals and plants which are of general biological interest. A more or less arbitrary choice of material has been made, and certain groups of substances, such as the purine bases, are entirely omitted. On the other hand, those which are included are given fairly full treatment, their physiological action as well as their chemical properties and constitution being adequately discussed. The practical methods of isolating and studying the bases which were employed by their discoverers and investigators are described, and the student will be able to gather from the monograph many suggestions as to fruitful research work.

Alloys and their Industrial Applications. By EDWARD F. LAW. Second Edition. London: Charles Griffin and Co., Ltd. 1914.

IN the second edition of this book the results of recent investigations are incorporated, and a thoroughly practical account is given of the properties and industrial applications of alloys. Methods of investigating alloys are clearly described, the details being sufficiently full for the purposes of students of metallurgy. The purely scientific research work which has been published recently in great abundance is not included, the book being intended chiefly for the practical man. Specially important alloys, such as brasses and bronzes and the iron alloys, are treated very fully, and some interesting new illustrations have been added to the second edition.

Metropolitan Water Supply. Extract from the Annual Report of the Local Government Board for 1912-1913. London: Printed under the Authority of His Majesty's Stationery Office by Darling and Son, Ltd. 1914.

THE results of the periodical inspections made by Mr. C. Perrin as Water Examiner under the Metropolis Water Act are contained in this report, and some account is given of the works in progress for the extension and improvement of the Metropolitan Water Supply. Dr. A. C. Houston's new method of using lime in the softening, purification, and sterilisation of water ("excess lime method") is also described. Many experiments have been carried out in investigating this method, and its advantages and disadvantages are very fully discussed. There appears to be no doubt that it enables flood water to be safely and speedily used, and that it absolutely eliminates danger from epidemic water-borne diseases.

The Utilisation of Solar Energy. By A. S. E. ACKERMANN, B.Sc.(Engineering), A.C.G.I., M.Cons.E., Assoc. M. Inst.C.E. London: The Society of Engineers (Incorporated). 1914.

THIS pamphlet contains a paper which was read before the Society of Engineers in April last, and which dealt with a subject of the highest importance both scientifically and commercially. It is probably not within the knowledge of the average man that water can be made to boil by the unconcentrated rays of the sun, and although a good deal is said of the necessity for husbanding the earth's store of fuel, it is perhaps hardly generally realised that by the end of the present century the problem of supplying mills and factories with fuel will have become acute in America and more so in Europe. This being so, these accounts of the official tests of sun-power plants are of peculiar interest. The author describes the early types of the Shuman plant, in the first of which no means of concentrating the sun's rays were employed; afterwards in the 1911 form of apparatus plane glass mirrors were used to concentrate the rays, while finally in the 1913 type of absorber parabolic mirrors are used (Shuman-Boys absorber). The official tests carried out with this latest form of apparatus are described in detail, and the results are remarkable enough to deserve the very serious attention of engineers. The

author writes in a temperate spirit, and the pamphlet is an important addition to our knowledge of a new means of power production.

First Report of the Departmental Committee on the Heat Test as Applied to Explosives. London: Printed under the Authority of His Majesty's Stationery Office by Darling and Son, Ltd. 1914.

THIS report gives the details of the Committee's work in connection with the standardisation of the apparatus and materials used in the Abel Heat Test for explosives. The preparation of the sample to be tested and the application of the test are described in full. All the apparatus is illustrated by diagrams drawn to scale, and the report contains a short account of the visit of the Committee to the "Centralstelle für Wissenschaftlich-technische Untersuchungen" at Neubabelsberg, when Prof. Will stated his views upon the question of stability tests for propulsive explosives.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

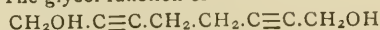
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 17, April 27, 1914.

Action of Chloroform on Metallic Sulphates.—Auguste Conduché. —Metallic sulphates are readily converted into anhydrous chlorides by vapour of chloroform at comparatively low temperatures. The following are the temperatures at which the reaction begins:— CuSO_4 , 250° ; NiSO_4 , 300° ; FeSO_4 , 300° ; MnSO_4 , 350° ; PbSO_4 , 350° ; $\text{Al}_2(\text{SO}_4)_3$, 400° ; MnSO_4 , 450° ; BaSO_4 , 500° ; CaSO_4 , 500° ; Na_2SO_4 , $>500^\circ$. At these temperatures, however, the transformation is slow and incomplete, and practically a higher temperature is necessary. At 400 – 500° , however, the chloroform itself decomposes, giving deposits of carbon, so that pure chlorides can be obtained only at low temperatures. In the case of copper the method is the best to employ for the preparation of the chloride.

Alkaloid obtained from Galega officinalis.—Georges Tanret.—*Galega officinalis* is a herbaceous leguminous plant which is much cultivated in France. The author has obtained from its seeds a new alkaloid which he calls galegine. It fuses at 60° to 65° ; it has no rotatory power, and is very soluble in water and absolute alcohol. Its formula is $\text{C}_6\text{H}_{12}\text{N}_3$, and the composition of its sulphate and of other salts shows that it is a monovalent base.

Preparation of Pure Butine.—M. Picon.—Pure butine can be prepared by the action of ethyl iodide upon monosodium acetylene. It is a colourless gas with an odour resembling that of pure carbon disulphide. The author finds that it boils at 8.3° under normal pressure, this being a much lower boiling-point than that previously ascribed to it. The gas is absorbed by all the reagents for true acetylenic hydrocarbons; it give a white precipitate with aqueous or alcoholic alkaline potassium iodomercurate, a white precipitate with alcoholic or ammoniacal silver nitrate, and a pale yellow precipitate with ammoniacal cuprous chloride.

Derivatives of 2.6-Octadiene-1.8-diol.—M. Lespieau.—The glycol function of—



is confirmed by the existence of a diacetic, and its unsaturated nature is proved by the fact that it fixes bromine and iodine. The product of hydrogenation is the saturated linear biprimary glycol $\text{C}_8\text{H}_{18}\text{O}_2$, which has been obtained by the hydrogenation of ethyl suberate.

MISCELLANEOUS.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 8th inst., The Duke of Northumberland, President, in the Chair. Mr. H. B. Hans Hamilton, Sir William H. Lever, Bart., Mr. Percy St. C. Matthey, J.P., Mr. H. W. P. Matthey, Miss Matthey, Mr. J. F. C. Snell, and Mr. T. J. Taylor were elected Members. The Chairman reported the decease of Sir Francis Laking and Sir Joseph Swan, Members of the Institution, and Resolutions of Condolence with the families were passed. The Secretary announced that His Grace the President had nominated the following gentlemen as Vice Presidents for the ensuing year:—Lord Blyth, Mr. J. H. Balfour-Browne, Mr. Charles Hawksley, Dr. Donald Hood, Lord Moulton, Mr. E. Pollock, Sir James Crichton-Brown (Treasurer), and Mr. Alexander Siemens (Secretary).

The Wellcome Historical Medical Museum.—The Historical Medical Museum, which was founded by Mr. Henry S. Wellcome in connection with the Seventeenth International Congress of Medicine, was re-opened on May 28th as a permanent institution in London. It is now known as the "Wellcome Historical Medical Museum," and is open daily from 10 a.m. to 6 p.m., closing at 1 p.m. on Saturday; entrance 54a, Wigmore Street, Cavendish Square, W. Since closing last October the collections in the Museum have been considerably augmented and entirely rearranged. Many objects of importance and interest have been added, which it is hoped will increase the usefulness of the Museum to those interested in the History of Medicine. Members of the medical and kindred professions are admitted on presenting their visiting cards. Tickets of admission may be obtained by others interested in the History of Medicine on application to the Curator, accompanied by an introduction from a registered medical practitioner. Ladies will be admitted only if accompanied by a qualified medical man.

MEETINGS FOR THE WEEK.

THURSDAY, 18th.—Royal Society. (1) "Trypanosome Diseases of Domestic Animals in Nyasaland, *Trypanosoma caprue* (Kleine)—Part III., Development in *Glossina morsitans*;" (2) Trypanosomes found in Wild *Glossina morsitans* and Wild Game in the 'Fly-belt' of the Upper Shire Valley; (3) Food of *G. o. sinu morsitans*; (4) Infectivity of *Glossina morsitans* in Nyasaland during 1912 and 1913," by Surg.-Gen. Sir D. Bruce, Major A. E. Hamerton, Capt. D. P. Watson, and Lady Bruce. "Relation between the Thymus and the Generative Organs, and on the Influence of these Organs upon Growth," by E. T. Hahn and F. H. A. Marshall (with a note by G. U. Yule). "Vapour-pressure Hypothesis of Contraction of Striated Muscle," by H. E. Roaf. "Validity of the Microchemical Test for the Oxygen Place in Tissues," by A. N. Drury. "Man's Mechanical Efficiency," by J. S. Macdonald. "Colouring Matters in the Compound Ascidian *Diazona violacea*," by A. Holt. Chemical, 8.30. "Nitrogenous Constituents of Hops," by A. Chaston Chapman. "The Isomerism of the Oximes—Part IV., Constitution of the N-methyl Ethers of the Aldoximes and the Absorption Spectra of Oximes, their Sodium Salts and Methyl Ethers," by O. L. Brady. "Wet Oxidation of Metals—Part III., The Corrosion of Lead," by B. Lambert and H. E. Cullis. "Studies in the Camphane Series—Part XXXV., Isomeric Hydrazoximes of Camphorquinone and some Derivatives of Aminocamphor," by M. O. Forster and E. Kunz. "Velocities of Combination of Sodium Phenolates with Olefine Oxides," by D. R. Boyd and E. R. Marle. "Colouring Matters contained as Glucoside in the Flowers of some Indian Plants," by A. G. Perkin and I. Shurlman. "A New Chlorocamphor," by T. M. Lowry and V. Steele. "Ideal Refractivities of Gases," by W. J. Jones and J. R. Partington. "Purification and Physical Properties of α -Bromonaphthalene," and "Determination of Water in Alcohol-water Mixtures by the Clouding Points of Mixtures with α -Bromonaphthalene," by M. Jones and A. Lapworth.

THE CHEMICAL NEWS.

VOL. CIX., No. 2847.

THE PREPARATION OF EYE-PRESERVING GLASS FOR SPECTACLES.*

By Sir WILLIAM CROOKES, O.M., F.R.S.

(Continued from p. 280).

Copper.

COPPER by itself as a constituent of glass is not of much advantage. It colours the glass blue, has not much action on the ultra-violet rays, but cuts off three-fourths of the heat rays. It forms a useful addition to other colouring agents in tending to neutralise those of the orange-yellow colour.

Iron (FeO).

Iron is introduced into the glass as ferrous sulphate, care being taken to avoid all oxidising agents. The fused mass is stirred with a carbon rod, and a little powdered charcoal added to the melt in the crucible. In quantities from 1 to 2.5 per cent the obstruction to heat radiation is great, and increases with the quantity of metal present. One per cent of iron cuts off about 65 per cent of the heat, and 2.3 per cent cuts off about 89 per cent. The action on the ultra-violet end is but slight, the photographs extending to λ 3467 with the lowest amount of iron, and to λ 3560 with the largest amount experimented with. The light transmitted by the 2 mm. plate is 71 per cent with the least amount of iron and 50 per cent with the largest amount. The colour of the glass is greenish blue. Iron in the ferrous state, therefore, will prove useful on account of its communicating adiabatic property to the glass.

Iron (Fe₂O₃).

In this state of oxidation iron glass cuts off ultra-violet light to a limited extent. When small proportions only are present, such as 0.25 per cent, the rays are transmitted from λ 3500 (far in the ultra-violet), and it is only when the amount of iron in the per state rises to about 2 per cent that the glass becomes opaque to the rays near λ 4000 (about the limit of visibility in the violet). A glass of this composition cuts off about 63 per cent of the total heat. The colour is almost pure yellow. The glass transmits about 75 per cent of the incident light. Iron in the per state, therefore, is another metal useful in combination.

Lead.

A plate 2 mm. thick was cut from a block of Faraday's "heavy glass" (boro-silicate of lead) prepared by himself, and tested as a sample of lead glass. It is practically colourless and transparent, and is opaque to the ultra-violet above λ 3800. Its action on the heat rays is slight, only cutting off about 38.5 per cent.

Manganese.

Glass containing manganese is of a reddish purple colour. In respect to obstruction to the ultra-violet and heat rays manganese has no special action. It has, however, been experimented with to obtain a neutral coloured glass by adding it to glass containing a greenish colouring agent.

Neodymium and Praseodymium.

These two bodies would be useful in the quest for a suitable glass were they to be obtained at a price which would not be prohibitive. In aqueous solutions praseodymium salts are greenish yellow, and those of

neodymium are of a violet-rose colour. Mixed together in the proportion of five parts of praseodymium to one of neodymium the mixture is of a neutral grey. In solid solution in glass the colours are—praseodymium greenish yellow, and neodymium lilac. Melted together in glass in the same proportion as in aqueous solution, the resulting colour is also neutral grey. In this respect these two elements differ from nickel and cobalt, inasmuch as the colours remain constant either in aqueous solution or melted in glass, and the proportion required to obtain neutrality of tint appears to be the same in each case.

Uranium.

Glasses were prepared containing from half a per cent of uranium to over 4 per cent. The colour of the glasses with smallest quantity of metal is very faint brown, and with the highest proportion it is yellowish brown. The opacity for ultra-violet light increases as the glass is richer in metal, the one with about 4 per cent uranium being opaque to the indigo and violet down to the blue. The heat absorbed at most is about 55 per cent. These results show that uranium is a metal likely to be useful in combination.

Composition of Glasses Specially Selected for Practical Use.

Whilst bearing in mind that the chief object of this research is to find a glass that will cut off as much as possible of the heat radiation, I have also attacked the problem from the ultra-violet and the transparency points of view. Taking each of these desiderata by itself I have succeeded in preparing glasses which cut off over 90 per cent of heat radiation, which are opaque to the invisible ultra-violet rays, and are sufficiently free from colour to be scarcely noticeable when used as spectacles. But I have not been able to combine in one specimen of glass these three desiderata in the highest degree. The ideal glass which will transmit all the colours of the spectrum cutting off the invisible rays at each end, is still to be discovered.

As far as transparency, however, is concerned it will not be an unmixed advantage for the sought-for glass to be quite clear and colourless. The glare of a strong light on white cliffs, expanses of snow, electric light, &c., is known to be injurious to the eye, and therefore a tinted glass combining good obstruction to the heat radiation and ultra-violet rays is the best to aim for.

Grey or neutral tints are the most pleasant to wear. They do not appreciably alter the natural colours of objects, and are a great relief to the eye. Many glasses are met with in commerce of different colours which are found by experience to suit the public demand for tinted spectacles. They are of various tints of yellow, green, blue, and neutral, and therefore I do not think it will be wrong to select the tints of my glasses, suitable in other respects, no darker than those which appear to suit the public taste.

As a basis for the preparation of the coloured glasses, Mr. Powell prepared for me a quantity of hard soda-flux mixture of the following composition:—

Sand	61.00
Sodium carbonate, anhydrous ..	25.50
Sodium nitrate, re-crystallised ..	5.00
Calcium carbonate, precipitated ..	7.20
Borax	0.75
Arsenic trioxide	0.55
	100.00

This mixture whilst melting loses about 25 per cent in weight. When first melted, it is colourless; on second melting it acquires the usual faint greenish tint of soda-lime glass. The contents of a large potful of the melted flux was poured into cold water. The broken-up mass was sent to my laboratory and has been used in the preparation of the test glasses. The object of pouring the molten flux into water is to break it up and render it easy to powder for convenience of adding other ingredients. In this state I call it "Fused Soda Flux."

* Read before the Royal Society, November 13, 1913. From the *Philosophical Transactions of the Royal Society*, Series A, vol. ccxiv., pp. 1—25.

Sometimes it is found advisable to use the flux in its raw state without previous melting, and when working upon the large scale this is the best plan. I then call it "Raw Soda Flux."

Without counting numerous preliminary experiments, I have made and fully tested over 300 tinted glasses, the quantitative composition of each being known. From these glasses I have selected a certain number which possess valuable qualities in respect of athermancy, adiatinity, and transparency.

I will now give the composition of these glasses, and the special properties in respect to the desired results.

Glass 150.

Fused soda flux	90.00
Cerium borate	8.13
Nickel sulphate, crystallised	0.07
Uranoso-uranic oxide	1.80

100.00

In Glass 150 a small amount of nickel has been added to the cerium and uranium. The colour is pale yellow, and it is opaque to ultra-violet radiation, the limit being λ 3613. It cuts off 37 per cent of the heat radiation and transmits 73 per cent of the incident light. The tintometer numbers are:—Red, 4.0; yellow, 3.5; blue, 0.5.

Glass 158.

Fused soda flux	89.75
Cerium borate	8.18
Ferroso-ferric oxide	2.03
Chromic oxide	0.09

100.00

This glass is pale greenish yellow. It is quite opaque to all the ultra-violet rays, the limit being λ 3700. It cuts off 63 per cent of heat radiation, and transmits 54 per cent of the light.

The glass has a pale greenish yellow colour. Its tintometer numbers are:—Yellow, 2.75; blue, 3.5.

Glass 165.

Raw soda flux	87.56
Cerium borate	8.00
Ferrous sulphate, crystallised	3.00
Uranic oxide	0.55
Nickel oxide	0.09
Chromic oxide	0.80

100.00

This glass cuts off practically all the ultra-violet rays shorter than λ 3680, and 38 per cent of the heat radiation. It transmits 48 per cent of the light. Its colour is a pale yellowish green. Its tintometer numbers are:—Yellow, 4.0; blue, 2.50.

Glass 187.

This glass and the next are both cerium glasses. No. 187 is composed of:—

Fused soda flux	83.0
Cerium nitrate, crystallised	17.0

100.0

The heat rays cut off by this glass are only 27 per cent, but its other qualifications are important. It is practically opaque to ultra-violet radiation, the limit being λ 3650, and it transmits 99 per cent of the light.

In the tintometer and opacity meter no colour or want of transparency can be detected, although against white paper in a good light a faint tinge of yellow is perceptible.

Glass 197.

Fused soda flux	79.00
Cerium nitrate, crystallised	20.50
Nickel sulphate, crystallised	0.30
Cobalt sulphate, crystallised	0.05
Uranoso-uranic oxide	0.15

100.00

Nickel and cobalt are here mixed in the proportion to make a neutral tinted glass, the other ingredients only slightly modifying the colour. The colour is a pale neutral. It is opaque to ultra-violet rays of shorter wave-length than λ 3700, and cuts off 41 per cent of the heat rays. It is transparent to 45 per cent of the incident light. The numbers in the tintometer are:—Red, 2.00; yellow, 3.00; blue, 5.50.

Glass 202.

I have obtained a neutral tinted glass by neutralising the orange-yellow colour communicated to glass by iron in the ferric state, by adding to it a little cobalt, which colours it blue. The composition is:—

Soda flux	95.15
Fe ₂ O ₃	4.75
CoSO ₄ .7H ₂ O	0.10

100.00

The resulting glass is opaque to ultra-violet of shorter wave-length than λ 3830, it cuts off 83 per cent of the heat radiation, and transmits 25 per cent of light. The tintometer numbers are:—Yellow, 2.5; blue, 5.5.

Glass 210.

Fused soda flux	89.0
Ferrous sulphate, crystallised	8.9
Chromic oxide	1.3
Carbon, in fine powder	0.8

100.0

Glass 210 is of a bluish green colour, the blue colour communicated by the ferrous oxide making the colour of the chromium not so pure a green. It cuts off all ultra-violet rays of shorter wave-length than λ 3620. It obstructs 87 per cent of the heat radiation, and transmits 30 per cent of light. The tintometer numbers are:—Yellow, 2.0; blue, 16.0.

Glass 217.

A further attempt was now made to get the iron in the ferrous state, and a glass was prepared of the following composition:—

Fused soda flux	96.80
Ferroso-ferric oxide	2.85
Carbon	0.35

100.00

A few percentages of finely powdered carbon are added to this mixture before fusion to keep the iron in the proto-state. Any excess of carbon rises to the top of the fused mass and prevents oxidation of the iron. This glass is of a pale blue colour, and cuts off the ultra-violet rays shorter than λ 3550. It cuts off 96 per cent of the heat radiation, and transmits 40 per cent of light. Spectacles made of this glass are very pleasant. The glass is bluish with a tinge of green. In the tintometer the numbers are:—Yellow, 2.0; blue, 8.0.

Glass 221.

Fused soda flux	80.0
Cerium nitrate, crystallised	13.4
Uranoso-uranic oxide	6.6

100.0

In this glass the action of uranium on the ultra-violet rays is added to that of cerium. The colour is faint yellow. It practically cuts off all the ultra-violet radiations, the limit being λ 3685, and it also cuts off 39 per cent of the heat rays. Its transparency is 60 per cent. In the tintometer the number is:—Yellow, 8.0.

Glass 238.

Raw soda flux	77.0
Cerium nitrate, crystallised	23.0

100.0

Glass 238 is similar in composition to Glass 187, but it contains more cerium. Like 187 it is practically opaque to ultra-violet light, the limit being about λ 3610, the injurious rays being beyond this wave-length. It cuts off 34 per cent of the heat, and transmits 71 per cent of the luminous rays. In the tintometer the numbers are:—Red, 0.375; yellow, 0.375; blue, 1.500.

(To be continued).

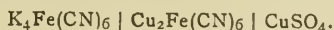
DIFFUSION AND MEMBRANE POTENTIALS.*

By E. B. R. PRIDEAUX, M.A., D.Sc.

WHEN two solutions of the same salt of different concentrations, or of different salts, are separated by a porous diaphragm, there is generally an e.m.f. set up at this which differs in magnitude from the diffusion e.m.f. at the junction of the same two solutions without any separate membrane.

In considering the possible cause of this potential, it would seem to be important to emphasise the distinction between those membranes which are capable of furnishing ions of the electrolyte and those which are not.

There is an essential difference between chemical precipitation membranes, such as those of copper ferrocyanide, and organic tissue membranes, such as parchment, collodion, or gelatin. The former kind may, as Beutner has pointed out, act to some extent like the AgCl and other electrolytically conducting solids investigated by Haber and Beutner; they form a reserve of ions and behave to some extent like metallic electrodes. Beutner, for example, observed an e.m.f. of 0.115 volt which remained steady for ten minutes in the combination:—



He supposes that this e.m.f. is due to the concentration fall between K^+ in the $K_4Fe(CN)_6$ and the small K^+ present in the $CuSO_4$. There is a small amount of double ferrocyanide of K and Cu in the membrane which is reversible with respect to K ions. If the $CuSO_4$ side is stiffened with gelatin, so as to prevent the diffusion into the body of solution of those K ions which are continually being produced on this side, then the e.m.f. drops to 0.003—0.010 volt.

This valuable hint as to the nature of $Cu_2Fe(CN)_6$ membrane was not available when the author commenced a series of researches which were devised to ascertain to what extent such a membrane hindered the motion of the ions of a salt—sodium benzoate—which as a whole diffuses through with great slowness. Although potentials were obtained with this solution, which, unlike those observed by Beutner, remained constant over long periods and also gave a regular alteration of e.m.f. with concentration gradient, yet the substitution of another membrane sometimes gave results differing from the former by far greater amounts than could be accounted for by experimental error. The anomaly could only be accounted for by the superposition of irreversible effects and effects of reactions with materials of the membrane, upon those due to the selective hindrances of ionic diffusion.

It was decided, therefore, to investigate those simpler cases in which the latter cause alone was likely to be operative.

This simplification is to be expected in the case of cellulose or other organic tissue membranes, which have a particular importance to physiological chemistry on account of their similarity to animal and vegetable membranes.

The e.m.f.'s observed in muscles, nerves, &c., have been assigned by Ostwald (*Zeit. Phys. Chem.*, 1890, vi., 71) to a selective permeability of ions. The effect may be divided into two parts;—

1. Hindrance of ionic motion due to the nature of the solid membrane.

2. Hindrance of ionic motion due to the sugars, starches, &c., which alter the properties of the solution within the membrane as compared with the solution outside.

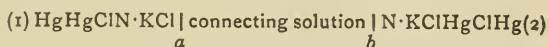
The following investigation obviously deals with the first of these effects.

The simple theory of an e.m.f. due to selective permeability of two ions through a membrane is of course merely an extension of the theory of diffusion potential. A diffusion e.m.f. is found for the membrane which is supposed to be due to the difference in the relative ionic mobilities in that medium as compared with the ionic mobilities in the solution. Little experimental work appears to have been done with the following definite objects:—

1. Ascertaining over what range of concentration, if any, a constant transport number of the anion in a membrane could be defined.

2. How far such transport number differs from that in the solution.

To a research on the diffusion potential due to sharp and mixed surfaces of separation Cumming (*Trans. Far. Soc.*, 1913, vii., 5) has added a note on the use of membranes. The symmetrical combination—



was rendered unsymmetrical by the interposition of a membrane at a while at b the liquids were mixed. If the membrane was parchment the electrode (1) on the side of the membrane was + to the other to the extent of 3 mv. when the connecting solution was HCl, and (1) was about 6 mv. — to (2) when the connecting solution was NaOH. With LiCl (1) was + to (2) by 0.6 mv.

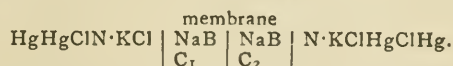
These results on the whole point to a strengthening of the diffusion potential by the membrane, i.e., to an exaggeration of the differences between the anion and cation mobilities. The difference between membrane and diffusion potentials gradually disappeared with time, indicating perhaps a gradual removal of the mixed layer from the membrane by diffusion.

In the following series of measurements parchment paper was chosen as the membrane material on account of its wide employment in chemical and biological researches, which gives a value to any additional knowledge of its properties.

A salt was required which should, as a whole, diffuse only slowly through the membrane, and which should not furnish any appreciable amount of H^+ or OH^- by hydrolysis. Sodium benzoate proved suitable in these respects. It was considered important to use a binary salt in order to reduce the uncertainty in the calculation of ionic concentrations.

The amount of sodium benzoate diffusing from a N/5 solution through parchment into pure water was found to be small. It was not sufficient to influence the e.m.f. in a day, if the weaker side was at least N/10. When there was N/2 solution on one side and N/100 upon the other a slow fall of e.m.f. with time was observed. In such cases the more dilute or both solutions were analysed immediately after reading the e.m.f.

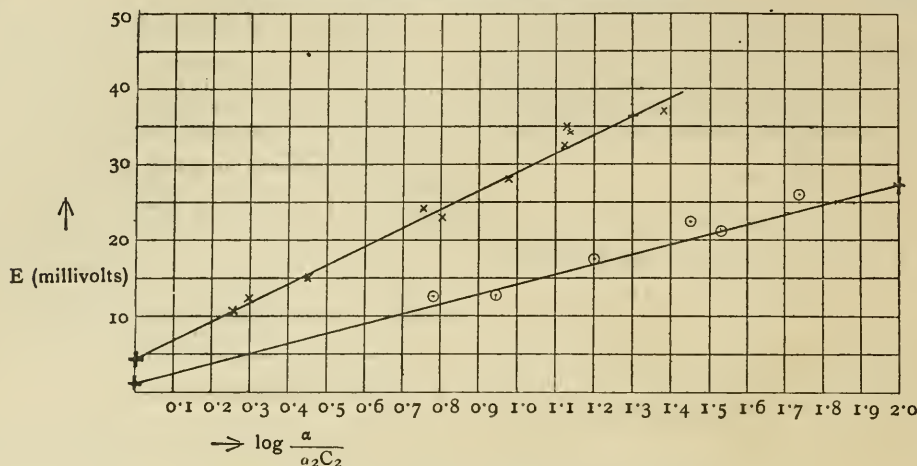
The combination actually used was—



The temperature variation of the membrane e.m.f. itself for variations of a few degrees in the neighbourhood of 18° was shown to be unimportant, that in the calomel electrodes is, of course, eliminated by their opposition. The quality in temperature of the two electrodes was in most cases checked by a measurement of the one against the other when they were connected by N·KCl.

The diffusion potentials of N·KCl against C_6H_5COONa at concentrations C_1 and C_2 was eliminated by a concentrated solution of potassium chloride (3.5 N). At present

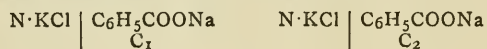
* A paper read before the Faraday Society, April 22, 1914.



ELECTROMOTIVE FORCE AND IONIC CONCENTRATION.

(o) (o) Diffusion e.m.f. x x Membrane e.m.f. + + Calculated from equation.

it cannot be stated certainly that the saturated KCl eliminated the diffusion e.m.f. at the junctions—



but the probability that these were either eliminated or brought to very low values, and their difference therefore almost eliminated, is strengthened by the result of the measurements of the diffusion e.m.f. of $\text{C}_6\text{H}_5\text{COONa}$ C_1 against C_2 .

The membrane was secured by rubber rings and metal clamps between two flanged glass tubes held horizontally, closed at the ends by stoppers containing glass tubes bent at right angles to make connection with the calomel electrodes. The e.m.f. became constant as soon as the combination was set up, whereas that of the copper ferrocyanide previously investigated often required half-an-hour or more to attain a steady value. The more dilute solution was in all cases positive.

Ionic Concentrations.

These were calculated from the molecular conductivities in the usual manner. The data in Kohlrausch and Holborn's "Leitvermögen" were supplemented by determination of conductivities from 0.1 N to 1 N.

The values at 25° are as follows:—

C = 1.0	0.5	0.2	0.1	0.05	0.02	0.01
$\lambda = 42.2$	52.6	62.0	67.2	70.4	74.5	76.5

interpolated.

The values of $[\text{Na}^+]$ or a_c as tabulated below were plotted against C and the values a_c in the table have been read off from this.

C = 0.01	0.02	0.05	0.10	0.20	0.50	1.00
$a_c = 0.0086$	0.0167	0.0395	0.0755	0.139	0.295	0.472

Diffusion Potentials.

The transport numbers of Na^+ and $\text{C}_6\text{H}_5\text{COO}^-$ in aqueous solution with which were to be compared those in the membrane may in the first place be determined from the data collected by Bredig (*Zeit. Phys. Chem.*, 1894, xiii., 191). From the ionic mobilities at high dilution of $\text{Na}^+ = 49.2$ and $\text{C}_6\text{H}_5\text{COO}^- = 31.2$, the transport number of the anion (n_A) is 0.388 and $1 - 2n_A$ is 0.224. It was desirable to supplement this by a determination of the average transport numbers in more concentrated solutions. This was done by measuring a series of diffusion potentials.

From the equation—

$$\text{Diffusion potential, } E_d = 0.058 (1 - 2n_A) \log \frac{a_1 C_1}{a_2 C_2}$$

the mean value of $1 - 2n_A$ could thus be determined.

The measurement was carried out in a similar manner to that of the membrane potential, the place of the membrane being taken by a syphon tube containing the more dilute of the $\text{C}_6\text{H}_5\text{COONa}$ solutions. No special care was taken to preserve a sharp boundary between dilute and concentrated solution, since, in the first place, no change of E was observed within a moderate time; such a change would have taken place if the progress of the mixing with time had been capable of producing it. Cumming (*loc. cit.*) also has been unable to detect any potential difference due to the opposition of a completely mixed and a sharp contact between two electrolytes.

The results indicate that the relation between E_d and $\log \frac{a_1 C_1}{a_2 C_2}$ is nearly linear, and that therefore there is a mean transport number which does not vary much with the dilution.

The e.m.f. between a 0.1 and 0.01 solution is, e.g., almost identical with that between 1.0 and 0.1 solution:—

E(mv).	C_1	C_2	$\log a_1 C_1 - \log a_2 C_2$
12.8	0.1	0.01	0.945
17.5	0.2	0.01	1.20
21.2	0.5	0.01	1.53
25.1	1.0	0.01	1.74
12.85	1.0	0.01	0.79
22.6	1.0	0.02	1.45

These results are shown by the lower line on the graph. The best linear equation connecting E and $\log \frac{a_1 C_1}{a_2 C_2}$ was calculated by the method of least squares, and it was found that—

$$E(\text{mv.}) = 1 + 13.5 \log \frac{a_2 C_1}{a_2 C_2}$$

On the above assumptions the linear graph should pass through the origin, actually it is +1 millivolt away. The average value of $1 - 2n_A$ is—

$$\frac{13.5}{58} = 0.234$$

and—

$$n_A = 0.383.$$

The transport number of the anion therefore agrees we

with that calculated from the ionic mobilities at infinite dilution, *i.e.*, 0.388.

Membrane Potentials.

The potentials observed when the diffusing layer is on a parchment membrane are considerably higher than the ordinary diffusion potentials, although they do not in any case reach the value $E(\text{mv.}) = 58 \log \frac{C_1}{C_2}$ corresponding to $n_A = 0$, or a membrane impermeable to the benzoic anion. On the above assumptions the effect of the membrane appears to be to decrease the mobility of the anion compared to that of the cation.

The relation of $\log \frac{a_1 C_1}{a_2 C_2}$ to E is here also approximately linear, and from it an average transport number in the membrane has been calculated.

The magnitude of the deviations may be seen on the accompanying graph. They may perhaps be due in part to the uncertainty in the calculation of ionic concentrations from conductivities. The theory has also been somewhat severely tested by the employment of such different ranges of concentration. Thus it has been assumed that a fall of ionic concentration between 0.5 and 0.05 will produce the same e.m.f. as the fall between 0.2 and 0.02.

In the following table the total concentrations of the two solutions are given in the first column, C_1 , C_2 . The second column contains the logarithms of the ratios of ionic concentration, the third the observed e.m.f. in millivolts:—

C_1, C_2	$\log \frac{a_1 C_1}{a_2 C_2}$	E (millivolts).
0.202—0.1007	0.26	10.80
0.505—0.209	0.30	12.20
0.202—0.064	0.44	14.95
0.202—0.025	0.81	23.05
0.505—0.064	0.76	24.20
0.202—0.0212	0.98	28.25
0.501—0.0252	1.125	32.60
0.505—0.0245	1.14	34.45
0.202—0.012	1.13	35.10
1.010—0.023	1.39	37.25

The numerical constants of the linear equation:—

$$E = a + b \log \frac{a_1 C_1}{a_2 C_2}$$

are found to be:—

$$E(\text{mv.}) = 4.53 + 24.8 \log \frac{a_1 C_1}{a_2 C_2}$$

Hence—

$$58(1 - 2n_A) = 24.8$$

and—

$$1 - 2n_A = 0.428 \quad n_A = 0.286$$

It is remarkable that this graph does not, as in the case of diffusion potentials, pass almost through the origin but intercepts an ordinate of 4.5 millivolts. Pending further investigation the author is unable to suggest an explanation of this. For zero difference of concentration the observed E falls to zero. It may be that the function assumes other forms between the smaller differences of concentration observed (about 2 to 1) and zero difference.

For such differences in concentration as lend themselves to measurement the transport number of the anion is apparently decreased in the ratio $\frac{0.286}{0.388} = 0.74$, *i.e.*, the transport

number of the anion in the membrane is less than three-fourths of that in the free solution.

Further work on similar lines will, it is hoped, decide the applicability of the above hypothesis to other cases, and also whether it is true in general that the mobility of the slower ion is apparently checked by such a diaphragm.

This work was done at the Muspratt Laboratory of the University of Liverpool in 1913.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

EXTRACTION OF GERMANIUM FROM THE WATERS OF VICHY.

In a recent study M. Jacques Bardet announced that germanium is to be found among the rare bodies contained in the water of Vichy. Since then he has undertaken the separation of this exceedingly rare body. The new researches, in which he gives the results obtained, have just been presented before the Academy by M. Moureu. In treating 100 kgrms. of the earthy residue which is precipitated during the evaporation of Vichy water employed in the manufacture of salts, 100 kgrms. of earthy salts correspond to 250 tons of mineral water. In proceeding by separations regularly followed with the spectrograph, so as not to lose this precious metal, the author has managed to obtain 6 centigrams. of pure oxide of germanium. This result corresponds to a proportion of 24 hundred-millionths of a milligram. per litre of water. This shows the sureness of the physico-chemical method in analysis. This kind of analysis may be compared to the extraction of radium, wherein also we proceed by separations, in following the operations with the electroscope. In the spectro-chemical analysis separations are also made, but they are followed with the spectrograph. Thanks to this new means it is possible to obtain infinitely small quantities of matters which it would never have been possible to isolate with the old methods.

TRANSMISSION TO A DISTANCE OF COLOURED PHOTOGRAPHY.

Telephotography is an invention of a relatively recent date. As is known, it consists in the transmission to a distance of photographs, drawings, plans, or sketches. Two different systems have been devised by Prof. Korn, of Munich, and by M. Edouard Belin, of Paris. An Italian engineer has tried to improve upon these methods. He has had the idea of transmitting telegraphically to a distance coloured photographs. His method consists in realising this transmission in three distinct and successive phases. In the first phase, for example, the orange-red colour will be transmitted, in the second green, and in the third the violet-blue colour. In this way the film of the receiving station will receive three different impressions in three separate times. This method can be realised in two ways:—(1) Either the coloured photograph will be placed on the turning drum of Korn's apparatus, this apparatus being lighted successively by a coloured source of the three different colours; or else (2) the photograph having been taken by means of an apparatus capable of obtaining in one single pose the images corresponding to the three fundamental colours, by successively transmitting these images lighted by white light. This method is also applicable to Belin's system of photography. For that it suffices to prepare three bichromated gelatin negatives, corresponding to the three fundamental colours, and to transmit them one after the other to the receiving station.

Institute of Metals.—Portsmouth Conference.—Portsmouth has been selected as the place of meeting for the Autumn Conference of the Institute of Metals. The Conference, which will be presided over by Engineer Vice-Admiral Sir Henry J. Oram, K.C.B., F.R.S., the President of the Institute of Metals, will be held on Thursday, September 10, and Friday, September 11, in the Municipal College, a number of important papers being read each morning. In the afternoon of September 10 a visit will be paid to Portsmouth Dockyard, and there will be a Dinner in the evening. On September 11 the afternoon function will consist of a Luncheon at the Cowes Works of Messrs. J. Samuel White and Company, the works afterwards being visited.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 28, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"Anomalous Trichromatic Colour Vision." By Prof. W. WATSON, D.Sc., F.R.S.

It is shown from the results of measurements made on some forty subjects that anomalous trichromates are sharply divided into two distinct classes, and two experimental methods of distinguishing these classes are described.

One class corresponds apparently to a reduction form of ordinary trichromatic colour vision, and is characterised by want of definiteness when making certain matches. The other class cannot be considered a reduction form of normal trichromatic vision, but corresponds to an abnormal type of trichromatic vision in that one of the sensation curves occupies a displaced position in the spectrum. Colour matches obtained by this class of anomalous trichromates differ from the normal, but the accuracy with which they can be made is as great as in the case of the normal.

A curious fact as to the first class is clearly brought out by the measurements recorded, namely, that in the matches described, although a considerable band of the spectrum supplies a satisfactory match to these persons, one limit of this band always corresponds to the position which gives a correct match for the normal, although the band lies sometimes on one side and sometimes on the other of this position.

"Diformdiol-peroxide." By Dr. H. J. H. FENTON, F.R.S.

The conditions of co-existence, and the mode of interaction, of hydrogen dioxide and formaldehyde are of some interest in connection with certain theories which have been advanced in order to account for the photo-synthesis of carbohydrates in the living plant. [Compare, for example, Bach (*Comptes Rendus*, 1893, cxvi., 1145), and Usher and Priestley (*Proc. Roy. Soc.*, 1906, lxxvii., 369, and lxxviii., 318)].

During the course of some experiments in this direction, it has been found that, under appropriate conditions, these two substances combine to form a compound $2\text{H}\cdot\text{CHO}\cdot\text{H}_2\text{O}_2$ which crystallises in large transparent plates or prisms. This compound explodes when warmed to about 75° , and takes fire if brought into contact with reduced iron or platinum black. It decomposes slowly in bright sunlight and appears to undergo some interesting changes, but it is stable if kept in the dark. In aqueous, or acetic acid, solution it gives the normal molecular weight for the formula indicated, and its condition at 0° , in aqueous solution, remains unchanged for forty-eight hours or more. If the aqueous solution is treated with platinum black the hydrogen dioxide is catalytically destroyed, and the freezing-point depression remains practically unchanged, indicating the dimeric form of the aldehyde, or else a corresponding mixture of the trimeric and monomeric forms (compare Aubach, *Chem. Centr.*, 1905, ii., 1031).

The general behaviour of the substance indicates that it is to be regarded as an "atomic" compound, in the ordinary sense of the term, rather than as a compound containing hydrogen dioxide of crystallisation.

It is most probable that the compound is identical with that which Legler, in 1881, obtained among the products of the slow combustion of ether.

*"Studies of the Processes Operative in Solutions. XXIX. The Disturbance of the Equilibrium in Solutions by**'Strong' and by 'Weak' Interfering Agents."* By Prof. H. E. ARMSTRONG, F.R.S., and E. E. WALKER.

The effect of a large number of substances on the optical rotatory power of an aqueous solution of fructose has been measured and the views put forward in No. XXVI. of these studies with regard to the action of interfering agents have been confirmed and elaborated. "Strong" solutes, such as the sugars and metallic salts, increase the negative rotatory power of fructose, whereas "weak" solutes, such as the alcohols, ketones, and ethers, decrease it. The observed effect of the added substance ("the interfering agent") is regarded as the algebraic sum of two opposing factors:—

1. A diluent effect causing dissociation of hydrates and other complexes in solution.

2. An influence, opposite in effect to the first, depending on the reciprocal chemical attractive powers of the molecules of solvent and interfering agents promoting association.

A simple mathematical expression involving these two factors has been developed by means of which (2) has been evaluated. This value is denoted by A. Thus calculated, A is found to be very nearly proportional to the number of atoms of oxygen in the molecule. The value of A, however, is increased by the presence of an ethylene linkage or of a phenyl group. In nitrogen compounds, A varies considerably with the mode of combination of the nitrogen. The same method of treatment has been adopted in analysing the influence of interfering agents on (1) the solubility of potassium chloride; (2) the rate at which cane sugar is hydrolysed by acids. The value of A is also correlated approximately with the influence which the solvent exerts on the rate at which chemical action takes place in solution.

"Morphological Studies of Benzene Derivatives. VII. The Correlation of the Forms of Crystals with their Molecular Structure and Orientation in a Magnetic Field in the case of Hydrated Sulphonates of Dyad Metals." By Prof. H. E. ARMSTRONG, F.R.S., and E. H. RODD.*"A Type-reading Optophone."* By E. E. FOURNIER D'ALBE, D.Sc.

A description is given of a new construction of the "optophone," an instrument capable of translating light action into sound, and so making light recognisable by means of the ear. The new instrument is intended to enable totally blind persons to recognise and "read" ordinary letterpress by means of the ear.

It consists essentially of a rapidly rotating disc perforated like a siren disc with several concentric circles of holes. A Nernst lamp is placed behind the disc with its filament stretched radially across the circles. The light, shining through the holes, gives regularly recurring flashes which, when of suitable frequency, can be detected by means of selenium and a telephone.

An image of this line of intermittently luminous dots is thrown upon the type to be read, and the light diffusely reflected from the type is received on a selenium bridge. As each dot has a characteristic note, the sound heard in the telephone will vary with every variation in the reflecting power of the surface under examination. As the letterpress is moved on in the direction of the line of type, the sound changes rapidly with every change in the shape of the letters, and with some practice the latter can be "read" by ear.

Type 5 mm. high can be thus read by means of an ordinary high-resistance telephone receiver. The effect becomes rapidly fainter as the type diminishes in size, but ordinary newspaper type is readable with the help of a highly sensitive Brown telephone relay.

"An Application of Electrolytically-produced Luminosity, Forming a Step towards a Form of Telectroscopy." By L. H. WALTER, M.A.

The author has investigated the conditions under which it should be possible to make practical use of the luminosity of anodes of alloyed aluminium forming part of a "valve" cell arrangement. The alloy known as "duralumin" is

found to give the best results, and with sodium tungstate solution as electrolyte, corrosion is practically eliminated when this alloy is used as the anode.

The difficulties with immersed anodes led the author to employ anodes which are completely dry, except as regards the front surface, which is kept wetted by means of a layer of electrolyte caused to flow down it in a continuous stream, the flow being distributed by using a transparent crêpe screen which clings to the anode surface. In this way, the anode being dry at the back, electrical connection can be directly established there, without the great care as to insulation otherwise needed.

This arrangement permits of the construction of an apparatus having a multiple anode, comprising a vast number of equal units in quite a small compass, each such unit being capable of being rendered luminous in any order or sequence desired and at a speed of some hundreds of times per second.

In the author's experimental apparatus there are over 5000 such separate units in a space the size of a cabinet photograph, or at the rate of over 24,000 per square foot—a number which it would hardly be possible to obtain by other means.

Such an apparatus is capable of being employed as a receiver in photo-telegraphy for the reproduction of pictures, &c., especially where these are received as electrical impulses. It constitutes a step towards one form of telegraphy, the luminous reproduction at some receiver, of an object visible at some distant electrically-operated transmitter.

"Axial Chromatic Aberration of the Human Eye." By P. G. NUTTING.

"Convection of Heat from Small Cylinders in a Stream of Fluid, and the Determination of the Convection Constants of Small Platinum Wires, with Applications to Hot-wire Anemometry." By L. V. KING.

CHEMICAL SOCIETY.

Extra Meeting, May 25, 1914.

Prof. W. H. PERKIN, Sc.D., LL.D., F.R.S., President, in the Chair.

THIS meeting was held in the Theatre of the Royal Institution, by kind permission of the Managers.

THE PRESIDENT, in opening the proceedings, said: We are assembled in this historic place to pay a tribute of respect to the honoured and revered name of Faraday, and, at the same time, to add another to the list of illustrious men who have served as Faraday lecturers in the past. I do not need to introduce Prof. Arrhenius to such a gathering as this. Many of you know him personally, and all of you are aware of the great influence which his brilliant and far-reaching generalisations have had on the development of modern science. I have therefore great pleasure in calling upon Professor Arrhenius to deliver the Faraday Lecture.

Prof. ARRHENIUS then delivered the Faraday Lecture, of which the following account is an abstract. (Full Report, *Trans.*, 1914, p. 1414).

MOST of my predecessors in this position, being mindful of the far-reaching importance of Faraday's discoveries, have treated general questions connected with Faraday's work, and bearing on our fundamental conceptions of matter. It is most opportune for me that the chief investigation made by myself falls within the great domain of electrochemistry, which Faraday enriched in a marvellous manner, especially by the discovery of his law, which is fundamental to all later work in this chapter of Science. The work on which I have to speak to you also concerns the constitution of matter. Solutions, especially those of salts, are of a peculiar character. Gay-Lussac, the most prominent physicochemist of his time, paid

special attention to solutions, and reached some conclusions which apparently are very modern. In his remarkable memoir of 1839, "Considérations sur les forces chimiques," he says: "As the effects of affinity do not change with temperature, whereas dissolution (solubility) is in a high degree dependent upon it, it is very difficult to avoid the assumption, that in dissolution as well as in evaporation, the product is essentially limited, at a given temperature, by the number of molecules which are able to exist in a certain volume of the solvent. They are separated from this, just as gaseous molecules are precipitated, by a lowering of temperature. . . . Dissolution is therefore in a high degree connected with evaporation, namely, in this respect, that both of them depend on the temperature and are subject to its variations. Hence they ought to show, if not a complete identity in their effects, at least a great analogy."

Here Gay-Lussac is a precursor of van't Hoff, who, forty-five years later, developed in such a masterly manner the idea of the analogy between matter in the dissolved and in the gaseous state.

In 1883 I investigated the electrical conductivity of different electrolytes, and came to the conclusion that the molecular conductivity increases with dilution, because the number of conducting molecules increases at the expense of the other, non-conducting, molecules. At infinite dilution all molecules of an electrolyte are conductors. This hypothesis led to the following chief conclusions. The molecular conductivity at infinite dilution is an additive property for all electrolytes, and not only within certain groups of electrolytes of similar composition, as maintained by Kohlrausch for the molecular conductivity of diluted electrolytes. According to the thermo-chemical data given by Berthelot and Thomsen, the stronger an acid is the greater is its molecular conductivity. The electrically conducting molecules are therefore the same as the chemically reacting molecules, the nature of which is characterised by Williamson and Clausius. At infinite dilution all acids must therefore be of the same strength. In accordance with these ideas, the velocity of reaction caused by an acid is proportional to its number of electrically conducting molecules per unit volume. This assertion could only be verified qualitatively in some very few cases, because experimental determinations were wanting. The heat evolved on neutralising one equivalent of an acid consisting of only conducting molecules with a base of similar kind is always the same and equal to the heat produced when one equivalent of conducting molecules of water is transformed into one equivalent of non-conducting molecules. Therefore the heat of neutralisation of strong acids with strong bases at high dilution, as in the experiments of Thomsen, when they are composed almost entirely of conducting molecules, is very nearly the same for all acids and bases in equivalent quantities. When a salt such as potassium ferrocyanide, $K_4C_6N_6Fe$, the ions of which are $4K$ and C_6N_6Fe , enters into a chemical reaction with another salt in aqueous solution, there are formed only ferrocyanides and potassium salts, but not ferrous or ferric salts, because the result is always a rearrangement of the ions.

Such were the conclusions drawn from a rather small number of experimental data, and I do not wonder that my colleagues refused to take notice of these ideas, which seemed absolutely incompatible with the prevailing conceptions regarding the chemical nature of salts. Very soon after my memoir had appeared, Ostwald published measurements of the conductivity of thirty-four acids, and showed that the molecular conductivity of the acids is very nearly proportional to the velocity of reaction in catalytic processes (inversion of sucrose, hydrolysis of esters) caused by these acids. A little later he also proved that the relative strength of weak acids, as compared with that of strong acids, increases with dilution, so that all acids show a tendency to become of equal strength in infinite dilution. Both of these laws were predicted in my memoir of 1884. Then there were two different phe-

nomena, the molecular conductivity and the chemical activity of acids, which quantitatively led to the same conclusion.

This was not, however, sufficient evidence to support the bold hypothesis that salts, including acids and bases, are to a great extent dissociated into their ions. Fortunately, I had not long to wait for further evidence. In 1886 van't Hoff published his revolutionising memoir on the analogy of dilute solutions to gases. There he showed that Raoult's measurements on the freezing point of aqueous solutions pointed to the fact that the influence of one molecule of a salt, such as potassium chloride, in great dilution, was double that of a simple molecule (alcohol, ammonia). This fact was wholly analogous to the fact that some substances, for example, ammonium chloride and phosphorus pentachloride, in gaseous state per molecule exert a pressure which is double as great as that produced by common undissociated gases. According to the law of Avogadro, the latter circumstance could only be explained by the hypothesis that the molecules of such substances as ammonium chloride or phosphorus pentachloride are dissociated, when vaporised, into two molecules, namely, ammonia and hydrogen chloride or phosphorus trichloride and chlorine, respectively. The experimental proof of this hypothesis was also given by v. Pebal and v. Than in 1862 and 1864. From analogy to this experience, there seemed no other possibility open to explain the abnormal freezing point of solutions of potassium chloride than to suppose that the molecules of this salt were for the greater part dissociated into their ions K and Cl. Thus Raoult's measurements of the freezing point gave a means of determining the degree of dissociation of a great number of substances, the aqueous solutions of which he had investigated. By the aid of the measurements of Kohlrausch, regarding the molecular conductivity of different substances, it was possible to make another independent determination of their degree of dissociation. The two methods gave values which agreed very well with each other when dilute solutions (generally 1 per cent) were examined. A thorough examination by A. A. Noyes and Falk (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 455) leads to the conclusion that for electrolytes consisting of two univalent ions the difference does not reach more than 2 per cent if the solutions are 0.1 normal or less. The same is also valid for potassium sulphate and lead nitrate. For salts such as calcium chloride, calcium nitrate, magnesium chloride, &c., the deviation is much greater, the freezing-point method giving too high values. The deviation seems to have something to do with the hygroscopic nature of most of these salts. For copper sulphate and similar salts I have found that the said method gives too low values, which is due to the formation of double molecules, as Hittorf observed as early as 1859. The change of the molecular composition with dilution is seen from the simultaneous change of the rate of migration. The chief point, however, is that salts (strong acids or bases included) consisting of two univalent ions give the molecular depression $2 \times 1.85 = 3.7$, salts of one bivalent ion with two univalent ions give $3 \times 1.85 = 5.55$, salts of one tervalent ion with three univalent ions give $4 \times 1.85 = 7.4$, &c., whereas non-electrolytes give 1.85, all in extreme dilution. In extreme dilution the dissociation is complete.

Further, it was possible to calculate the degree of dissociation from the strength of the catalytic action of the acids, and in 1889 I showed that, within the limits of the errors of observation, the values found in this manner agree wholly with the values deduced from the magnitude of the electrical conductivity.

Of the three methods of determining the degree of electrolytic dissociation, that founded on the measurement of the electrical conductivity has always been preferred to the other two. This choice is chiefly based on practical reasons, because the method is applicable to solutions in all solvents, and because it is possible to determine the conductivity with an accuracy of about 0.2

per cent up to the highest dilutions investigated—about 0.0001 normal. The high dilutions are just those by which the trustworthiness of the theory ought to be controlled.

There was also a fourth fundamental fact in favour of the dissociation theory, namely, the additive properties of solutions of electrolytes. Certainly there are other additive properties valid also for non-dissociated substances; for example, the mass of a substance is an absolute additive property, because it is equal to the sum of the masses of the constituents. If we except the mass, however, the additive character is far less prominent for undissociated molecules than for electrolytes.

The additive properties of solutions of electrolytes have for a long time attracted the attention of physico-chemists, because they are so strongly pronounced. If the electrolytes are dissociated into their ions, it is quite clear that the properties of their solutions may be regarded as the sum of the properties of the solvent and of the ions. The additive property which is most familiar to the chemist, is the chemical reaction of solutions of electrolytes. All salts containing chlorine as ion give the reaction "of chlorine," as it is said, but it would be more exact to say "of the chlorine ion." But chlorates containing the ion ClO_3 , perchlorates with the ion ClO_4 , the numerous chloro-salts of cobalt, platinum, iridium, &c., in which the chlorine is placed in the inner sphere, according to Werner, and all the salts of the chloro-substituted organic salts, do not give "the reaction of chlorine."

On these four strong foundations: the freezing-point, the electrical conductivity, the chemical reactions and other additive properties of electrolytic solutions, as well as the strength of acids and bases, it was possible to erect a thoroughly solid building capable of sustaining attacks from without, and this building is the theory of electrolytic dissociation, first enunciated in 1887.

As a general conclusion, it may be stated that the difficulties inherent to the theory of electrolytic dissociation have been overcome only within a very recent period, when the observed facts have been more closely examined. It is now our task to investigate the causes which interfere with the simple laws in more concentrated solutions, and to find those other theoretical laws which govern these deviations.

In presenting the Faraday Medal to Prof. Arrhenius at the conclusion of the lecture, the PRESIDENT said: Prof. Arrhenius, it is now my very pleasant duty to hand you the Faraday Medal, the highest honour the Society has to confer, and I should like to add an expression of our deep regard for you as an honoured member and our respect for you as a man of science.

Sir WILLIAM CROOKES, in proposing a vote of thanks to the lecturer, said: Mr. President. Ladies and Gentlemen,—With deep satisfaction I rise to propose a vote of thanks to our distinguished guest, and to offer our congratulations to him on his very interesting lecture. Prof. Arrhenius has made his subject glow. He has drawn freely upon his vast stores of knowledge, and he invites us to share in the astonishing results of his researches. We are glad to welcome him in this country, where, indeed, he is already well known, and glad to felicitate him upon his command of our language, and on the fluency which is so marked a feature of his speech. We find it peculiarly fitting that the Faraday Lecture should be delivered by the Director of the Nobel Research Institute.

There is perhaps no need for me to remind you of Prof. Arrhenius' scientific work. It is known to many how, more than a quarter of a century ago, he contributed to science one of its greatest generalisations, which he has now placed before you here, and which, after much strife, has taken its place as one of the corner-stones of chemistry. In early days I well remember the hostile objections. The hot controversies that raged reminded one of one of Ruskin's whimsical sayings—that most matters of

any consequence are not merely to be regarded from two points of view, but are really three- or four-sided, or even polygonal, and "trotting round a polygon is stiff work for people who are in any way stiff in their opinions."

We can hardly listen to a Faraday Lecture without letting our thoughts dwell upon the great Faraday himself, and comparing him and his work with that of his eulogist, our illustrious guest. Faraday's work, like that of Arrhenius, lay chiefly in the borderland of chemistry. He was the pioneer in the region of physical chemistry, which of late years has revealed such boundless stores of wealth. There is an obvious close connexion between his electrochemical laws and Arrhenius' theory of electrolytic dissociation. Faraday was a true epoch-maker, and a most striking example of the supreme value of those who cultivate science for its own sake without ulterior motives and without thought of the commercial value of their discoveries. How enormous is the value of Faraday's work the world has not yet by any means realised, but if in later times an adequate appreciation of its far-reaching results comes to be written, I am almost tempted to suggest that its title might be "Civilisation in the Making."

Arrhenius has suggested to us how worlds may be made, and surely Faraday did more than any one single individual to show us how to civilise worlds when made. A further resemblance may be observed between our guest and Faraday, and that is the remarkable gift of clear exposition. Not many of those present, I suppose, ever heard Faraday lecture; but some of you know of his fame in exposition, and I can assure you from personal experience that it has not in the slightest degree been exaggerated.

Prof. Arrhenius' later work in immuno-chemistry, and his researches into the action of toxins and anti-toxins, have challenged the attention of the scientific world, and still more recently his investigations in cosmogony have startled staid scientific men. "Worlds in the Making" is a title bound to catch the mind's eye, and those of you who have read the book, and the later volumes on the Life of the universe, will no doubt agree with me as to the absorbing interest of the subject, the cogency of the arguments, and the skill with which they are handled. The world is deeply in need of researchers both of the type of those whose genius is characterised by that fertility of resource in experimental investigation exhibited by Faraday, and of the type of Arrhenius, whose gifts of intrepid speculation and imagination enable him to reveal new worlds of thought. Both are revolutionaries and founders of new kingdoms. Both types are rare. Both are "world compellers," and the world's debt to them is incalculable. I think we may begin to look hopefully forward to a time of fuller recognition of scientific genius and deeper appreciation of the value of scientific work, and certainly the British nation will not be found in the rear-guard in that desired advance. Once again let us offer our hearty thanks to Prof. Arrhenius, and assure him of our genuine appreciation of his masterly exposition of, I might almost say, a sensational chemical problem.

Sir WILLIAM TILDEN, in seconding the vote of thanks, said: Ladies and Gentlemen,—I am one of those who cling tenaciously to the principle of submission to properly constituted authority. Consequently, when the President preferred a request that I should stand in this honourable position of seconding the vote of thanks to the Faraday Lecturer, which has been so eloquently proposed by the President of the Royal Society, I looked upon it as a command, and concealed my own misgivings, feeling as I did that I could not be regarded as a representative of any body of chemical opinion on the present occasion. We are here to-day to celebrate the great name of Faraday. A celebration of the same kind has been held by the Chemical Society on, I think, ten previous occasions, and it would be impossible, as you realise, no doubt, for the Society effectively to carry out its wish except with the aid of our eminent colleagues and

friends who have visited us from abroad on all these previous occasions.

We have had assistance from France, from Germany, from Italy, and from the United States. On the present occasion we have the great pleasure of welcoming among us, not for the first time—for his face and figure are familiar to everybody in London—we have the great pleasure of receiving here to-night and welcoming a representative of that great country which, I am almost tempted to say, has done more—but at any rate has contributed not less—than any other country to the advancement especially of chemical science.

It is only necessary to remember that Scandinavia has produced Scheele and Berzelius, besides many others whose names will doubtless occur to you. I think you will agree with me that our friend who has just delivered the Faraday Lecture is a worthy successor to his great countrymen whose names I have just mentioned.

I think the first qualification in a Faraday Lecturer must be that he has by his own work and his own researches contributed to the advancement of that department of science with which Faraday's name is, and has always been, associated; and in this case that quality is presented eminently by the Faraday Lecturer.

With regard to the theory of electrolytic dissociation, which has been the subject of the discourse this evening, my experience, perhaps, is very much that of a good many others, and probably the majority, in this room. When it first began to be discussed seriously, close upon twenty years ago, I confess I was among those who were strongly hostile. But I felt, as time went on, that I had to lay before my students—for I was a teacher in those days—at any rate an exposition of what other people believed in regard to this department of the theory of chemistry; and it was my experience that by merely presenting those views, so new and so unacceptable as they were to me at that time, I gradually got to feel that they were inevitable, and that they were absolutely necessary. One was forced to consider all the pros and cons, and ultimately I was led to a conviction of the very valuable character of the theory that I was then expounding. Of course, the theory of electrolytic dissociation, like every other theory which has become established in the fabric of theoretical chemistry, must pass through, has passed through, and will continue to pass through the same kind of experience as other theories. It has met, first of all, strong opposition and violent criticism, but it has ultimately been accepted, and all that remains is to clear away the few comparatively small difficulties.

At the same time, I always feel, and I hope most teachers feel, that every theory which we accept is bound to be modified more or less as time goes on. If not actually abolished, it will at any rate be modified very considerably in favour of something which is more comprehensive, and perhaps illuminated by a large number of new facts at present unknown to us.

I need scarcely say that I thank the President for allowing me the distinguished honour of standing here on this occasion, and I support most cordially the proposition which has been laid before the meeting by the President of the Royal Society.

The CHAIRMAN having put the vote to the meeting, it was carried with acclamation.

Prof. ARRHENIUS, in acknowledging the vote of thanks, said: Amongst learned societies, the Chemical Society was one of the very first which lent me support and gave me encouragement. It has therefore been a great pleasure and favour to me to come back to London on repeated occasions and speak to and see my many dear friends in this Society. Every time I returned I felt that your kindness and friendliness towards me had increased. To-day it has reached its maximum, when you have conferred upon me the greatest honour you can give. I cannot express my deep feelings of gratitude towards the Society as I would wish, and I must confine myself to saying that you have my warmest and deepest thanks.

SOCIETY OF PUBLIC ANALYSTS AND OTHER
ANALYTICAL CHEMISTS.

Ordinary Meeting, June 3, 1914.

Mr. LEONARD ARCHBUTT in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. John Kent Crow, 43, Westcombe Park Road, Blackheath, S.E.; and Horace Pinnemore, Pharmaceutical Laboratory, Guy's Hospital, S.E.

Certificates were read for the second time in favour of Messrs. William Roscoe Hardwick; Harold Fletcher Hills; and Robert Hindle Kay.

The following papers were read:—

"Insoluble Bromide Value of Oils and its Determination." By ALEXANDER GEMMELL.

The author gives an account of work carried out to obtain concordant results of this value. His conclusions are that the glycerides should not be directly brominated, but that an ethereal solution of the fatty acids should be used. The bromine content of the precipitates obtained has also been investigated, and he shows these to consist essentially of mixtures of bromo derivatives, not of pure hexa-bromides. The value determined for various oils is also given.

"Determination of Iridium in Platinum-iridium Alloys." By C. O. BANNISTER and E. A. DU VERGIER.

Gives details of a method of differentiating between platinum, platinum-iridium, and platinum-rhodium alloys by noting the appearance of beads obtained by cupelling small quantities of the materials with silver. The presence of rhodium is indicated by a large amount of spitting of the bead, and the presence of iridium by the fact that the bead assumes a more spherical shape, whilst the surface is seen under a low power microscope to be covered with markings indicative of internal stresses.

The results of the determination of the solubility of platinum-iridium alloys in aqua regia are given for a series of alloys containing from 2.5 to 25 per cent iridium.

Two methods for the accurate determination of iridium in platinum-iridium alloys are described and results obtained by these methods are compared.

The first method consists in cupelling with silver, parting with sulphuric acid to obtain separate particles of iridium and platinum, and then dissolving the platinum in dilute aqua regia and weighing the iridium. The second method consists in melting the alloy with pure lead, dissolving the lead in nitric acid, and separating the platinum and iridium as before with dilute aqua regia.

"Symbolical Representation of Analytical Operations." By L. GOWING SCOPES.

A scheme is proposed for representing analytical processes by means of symbols somewhat similar in application to chemical equations. A list of useful symbols is given, and several typical operations are worked out. Its probable uses and extensions are indicated.

"The Properties of some Chlorhydrocarbons and their Uses in Chemical Analysis." Part II. By L. GOWING SCOPES.

The author discusses the reaction between chloroethanes and phenylhydrazine. He finds the conditions vary too much to use the reaction for estimating these bodies, with the exception of hexachloroethane.

A method is given for the estimation of the chloroethanes by the action of $n/3$ alcoholic potash in the cold and the subsequent titration of the halide formed. Under these conditions hexachloroethane does not react and the chloroethylenes do not interfere.

A colorimetric method for estimating hexachloroethane is under investigation.

"Changes in the Character of Fats during the Process of Cooking." By HELEN MASTERS and HENRY L. SMITH.

When fats are cooked with flour, as in pastry, hydro-

lysis of the fat is but slight, changes of the same type as in the blowing of oils, however, occur. The iodine value decreases, the acetyl value and the refractive index increase. Apparently the fat becomes more hydroxylated, but no definite ratio between the decrease in the iodine value and the increase in the acetyl value can be observed. Oxidation of the fat also takes place, the fat becomes darker and more viscous and "oxidised" acids are formed. All these changes are more marked the longer the pastry is cooked. These changes have been observed with cotton-seed oil and butter-fat, butter-fat changing less than the more unsaturated oil. In the case of cotton seed oil there is also a marked increase in the volatile acids. Except in the case of very thin pastry or when it has been overcooked the changes are small, and would not interfere with the detection of adulteration or substitution.

"Chief Cause of the Loss on Sulphuric Anhydride and of Chlorine by Ashing Substances containing these Constituents." By JAMES O'SULLIVAN.

The author finds (1) that when either sulphate of calcium, potassium, or sodium are present with organic matter, an ash is obtained containing only slightly less sulphuric anhydride than was present, but if magnesium sulphate is present then the ash contains only a small proportion of the sulphuric anhydride; (2) that in the presence of magnesium sulphate and organic matter the chlorides may be completely destroyed; (3) the presence of phosphates has no influence on the amount of sulphuric anhydride found in the ash; (4) that if the ash of a substance is alkaline and contains magnesium oxide and no carbonate, then neither the chlorine nor the sulphuric anhydride found in it can be safely taken as anything like a measure of either of these present in the substance.

"Note on the Presence of Sulphates in Flour." By R. A. CRIPPS and A. G. WRIGHT.

The purport of this note was to show that sulphates exist as such in flour; direct determination in samples yielded 0.0069, 0.0076, 0.0084, 0.0084, 0.0069, and 0.0103 per cent, the last being a "whole-meal" flour.

The reason for the low results obtained by determination in the ash was stated to be the action of the acid phosphates of the flour upon the sulphate (or sulphide) at the low red heat required for ignition, experiments with the potassium acid phosphates mixed with sulphate of potassium or calcium indicating the complete volatilisation of the SO_3 .

The proof of presence of sulphates naturally in flour might be of considerable importance in legal cases of addition of "improvers."

NOTICES OF BOOKS.

Modern Steel Analysis. By J. A. PICKARD, B.Sc. (Hons. Lond.), A.R.C.Sc., A.I.C. London: J. and A. Churchill, 1914.

THIS little book will be useful to those who want concise directions for determining the most important constituents in steels; it is written for the practical man, and contains no superfluous details or lengthy discussions of trifling modifications of procedure. A short introductory section deals with general methods and gives some hints for economising time and saving labour in analysis; various pieces of apparatus which the author has found useful are described, and methods of sampling are briefly treated. In the special part the author has employed the space at his disposal judiciously, giving alternative methods for constituents of greater importance; in all cases rapidity of performance is taken into consideration in recommending certain estimations. The methods recently worked out by the author for cobalt, which is now being used for high speed steels, are described, and the many hints embodying the results of the author's personal experience of the processes described will be useful to the inexperienced analyst or student.

Clean Water and How to Get It. By ALLEN HAZEN. Second Edition. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1914.

THIS book gives a readable account of the means adopted in many American cities to obtain a pure water supply. Some account is also given of methods of purification, the storage of filtered water, and the use and measurement of water. The information relates chiefly to American processes, but some questions of general interest are discussed, and the results of American experience are compared with that of European engineers and sanitary authorities. In the new edition chapters have been added on red water troubles and how to prevent them and upon the disinfection of water supplies.

Trade and Technical Education in France and Germany. London: P. S. King and Son. 1914.

THIS report by Mr. J. C. Smail, Organiser of Trade Schools for Boys, describes the author's personal observations and investigations of the state of professional trade education in Paris, Munich, Leipzig, and Berlin. Mr. Smail spent some time in each of these cities, studying the different systems of technical education, and was given every facility to make himself thoroughly acquainted with the scope and working of the trade schools. His conclusions are particularly interesting, and deserve careful consideration on the part of educational authorities. Syllabuses of the courses of instruction are given in the report and details of the training of special teachers. The excellent results of the system of compulsory continuation classes in Germany are pointed out, and it is shown that the cost per student hour of the same kind of instruction does not materially differ in Paris, Munich, Berlin, and London.

Röntgen Patterns of Boracite obtained above and below its Inversion Temperature. By Prof. H. HAGA and Prof. F. M. JAEGER. Amsterdam: The Royal Academy of Sciences. 1914.

THIS paper gives a short account of the apparatus used by the authors in studying the transmission of Röntgen rays through plates of boracite crystal at different temperatures, and describes the results of experiments in which the time of transmission was from two to three hours, and the temperature was raised to about 300°. Plates are given illustrating the patterns obtained at 18° and at 303°, and the significance of the results is very briefly discussed.

Blowpipe Analysis. By NICHOLAS KNIGHT. Fifth Edition. Mount Vernon, Iowa: Cornell College. 1914.

THESE notes on blowpipe analysis contain explicit directions for the detection of bases by flame tests and by ignition on charcoal before the blowpipe. The author gives beginners many hints which will prevent them from falling into common errors, and equations are added when the reactions are at all complex. Wet tests for acids are also given, including some common organic acids. The notes will be very useful for elementary students, for whom they will provide a good foundation for more detailed and difficult work in qualitative analysis.

Stereochemie. ("Stereochemistry"). By Dr. E. WEDEKIND. Second Edition. Berlin and Leipzig: G. J. Göschen. 1914.

THE science of stereochemistry has made very rapid advances since 1904, when the first edition of this little work was issued, and it has been found necessary to revise many of the details and add very considerably to the information given in it. In its present form it is a convenient little handbook in which the fundamental principles of the subject are clearly explained. All the most recent advances are discussed, as for example the stereochemistry of pentavalent nitrogen and the work of Werner on the optical activity of inorganic compounds, and the book undoubtedly supplies a need for a thoroughly scientific and concise treatment of stereochemistry.

Rothamsted Experimental Station. Annual Report for 1913. By E. J. RUSSELL, D.Sc., Director. Harpenden: D. J. Jeffery. 1914.

THIS annual report contains accounts of the work done on the farm and in the laboratory and pot culture house at Rothamsted during the year 1913. The research work which has been brought to a satisfactory conclusion and published includes a method of estimating carbohydrates, especially in plant extracts, by Messrs. Davis and Daish, and investigations of the soil solution and the mineral constituents of the soil, while further work has been done on the sterilisation of the soil and the growth of plants in partially sterilised soils. The Director of the Station, Dr. E. J. Russell, wishes to draw attention to the fact that the Lawes and Gilbert Centenary Fund is not yet closed, there still being £950 to raise before the new laboratories can be built, and the Committee is particularly anxious to clear off this last sum and begin building operations at an early date. The value and importance of the work which has been and is being done at Rothamsted can hardly be overestimated, and the data which have been accumulated there have no counterpart anywhere else in the world.

Principes d'Analyse et de Synthèse en Chimie Organique. ("Principles of Analysis and Synthesis in Organic Chemistry"). By M. HANRIOT, P. CARRÉ, A. SEYEWETZ, E. CHARABOT, and A. HÉBERT. Paris and Liège: Ch. Béranger. 1914.

THIS book is volume v. of the Encyclopædia of Applied Chemistry which is in course of publication under the editorship of Professor C. Chabrie, of the Sorbonne, and for the preparation of which some of the most distinguished of French chemists have collaborated. The aim of the authors has been to discuss and explain general ideas and principles rather than to enter upon minute descriptions of the details of processes, and each section has been written by an expert who has specialised in the branch which he discusses. The general principles of analysis are treated by M. Hanriot and the properties and preparation of pharmaceutical products by M. P. Carré. The chapters on the synthesis of dyes have been written by M. A. Seyewetz, and give a fairly detailed account of general and special methods of preparation. The extraction of perfumes and the production of artificial perfumes are also treated and a short section is devoted to the study of saponification.

La Silice et les Silicates. ("Silica and the Silicates"). By HENRY LE CHATELIER. Paris: Hermann et Fils. 1914.

THIS treatise on silica and the silicates gives a detailed account of the chemistry of these important compounds. The chemical properties of silica and its hydrates are first described, and the following chapters deal with the physical properties of quartz, polarisation, double refraction, &c., being discussed at great length, while other forms of silica are treated rather more shortly. The general properties of different glasses are subsequently described, and chapters are devoted to the metallic silicates, which are admirably treated from a descriptive point of view. A discussion of the scientific aspects of the ceramic industry occupies another chapter. Details of manufacturing processes are not included, but a general outline of the principles upon which they are based is provided.

Rapport sur l'Unification des Abréviations Bibliographiques dans les Mémoires de Chimie. ("Report on the Unification of Bibliographic Abbreviations in Chemical Memoirs"). By Prof. Ph. A. GUYE. Geneva: Albert Kundig. 1914.

THERE is probably no need to call attention to the many advantages which would follow the adoption of a uniform system of abbreviation of the titles of journals, and the report of the proceedings of the third session of the "Association Internationale des Sociétés Chimiques," held

in Brussels at the Solvay Institute in September, 1913, will undoubtedly win the hearty approval of chemists. After some short discussion of the anomalies and difficulties involved. Prof. Guye details the proposal of the Council to invite the co-operation of editors and authors in the adoption of a uniform system of abbreviation of titles, and explains briefly how it is proposed that the Council should join with the Council of the International Catalogue of Scientific Literature to draw up a suitable and convenient list of abbreviations which, when accepted, will henceforward be regarded as international.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de France.
Vol. xv.-xvi., No. 8, 1914.

Specific Rotatory Power of Camphor Dissolved in Olive Oil.—Henri Malosse.—The specific rotatory power of camphor in olive oil increases with the dilution. If q is the number of grms. of oil in 100 grms. of solution the increase is almost negligible when q lies between 75 and 83, slow if q lies between 83 and 90, more rapid if q lies between 90 and 25, very rapid if q is >95 .

Composition of Gaseous Mixtures Resulting from the Action of Water on Carbides of Uranium and Thorium.—P. Lebeau and A. Damiens.—With the same sample the action of water upon the carbides of uranium and thorium gives comparable quantities of gaseous mixtures of very similar composition. With a graphitic and a non-graphitic carbide of uranium, however, the results are very different. In the latter case the reaction takes place much more slowly, and the hydrogenation of the hydrocarbons is more complete, as is shown by the increase in the proportion of hydrocarbons and the diminution of the quantity of hydrogen.

Action of Water upon Carbides of Rare Earths.—A. Damiens.—When water acts upon the carbides of cerium, lanthanum, neodymium, praseodymium, and samarium no methane is formed, the hydrocarbons obtained being acetylene, allylene, vapours of heavier hydrocarbons, ethylene, and ethane. The liquid hydrocarbons formed very readily fix oxygen in the cold. The systematic study of the oxides shows that they are the hydrates of sesquioxides, and the reaction takes place according to the equation $C_2M + 3H_2O = M(OH)_3 + C_2H_2 + H$. The hydrogenation of acetylene gives ethane and ethylene.

Products of Incomplete Reduction of Ceric Oxide.—A. Damiens.—The reduction of ceric oxide by carbon takes place in three stages:—

- (i.) $CeO_2 + C = Ce_2O_3 + CO$.
- (ii.) $Ce_2O_3 + 9C = 2CeC_3 + 3CO$.
- (iii.) $CeC_3 = CeC_2 + C$.

The compound described by Sterba as an oxycarbide does not appear to possess the formula, $CeC_{2.2}CeO_2$, which he ascribed to it. The author obtained red products which are mixed crystals of the carbide CeC_3 and of fused cerous oxide.

Atti della Reale Accademia dei Lincei.
Vol. xxiii. [i.], No. 7, 1914.

Modification of Kjeldahl's Method.—L. Marino and F. Gonnelli.—The modification of Kjeldahl's method proposed by Oefele leads to inaccurate results for the percentage of nitrogen, the found and theoretical values differing by as much as 1 per cent. The authors find that

more accurate results are obtained by boiling the organic substance (about 1 grm.) with 20 cc. of concentrated sulphuric acid in presence of about 7 grms. of potassium sulphate and 0.2 grm. of V_2O_5 , until an emerald green solution is obtained.

MISCELLANEOUS.

Presentation.—Dr. F. B. Power, Director of the Wellcome Chemical Research Laboratories, was the recipient of an interesting presentation on June 5. This took the form of an illuminated address, the design of which was based upon a very beautiful folio in a Fourteenth Century manuscript copy of the Wyclif Bible. The presentation was made by Mr. G. E. Pearson on behalf of the leading members of the staffs of the scientific and commercial enterprises which owe their initiative to Mr. Henry S. Wellcome. The address, which tenders the congratulations and good wishes of the donors on the occasion of Dr. Power's receipt of the honour of the Hanbury Medal, was accompanied by an exquisitely bound blue morocco volume of autographs.

MEETINGS FOR THE WEEK.

THURSDAY, 25th.—Royal Society. "Note on Mr. Mallock's Observations on Intermittent Vision," by S. P. Thompson. "Variation of Electrical Potential across a Semipermeable Membrane," by F. G. Donnan and G. M. Green. "Potential of Ellipsoidal Bodies and the Figures of Equilibrium of Rotating Liquid Masses," by J. H. Jeans. "The 27-Day Period in Magnetic Phenomena," by C. Chree. "Electrification of Water by Splashing and Spraying," by J. J. Nolan. "Attempts to produce the Rare Gases by Electric Discharge," by T. R. Merton. "Analysis of Gases after Passage of Electric Discharges," by O. C. G. Egerton.

ERRATUM.—P. 288, col. 1. In "Action of Chloroform on Metallic Sulphates," line 8, for " $MnSO_4$, 450," read " $MgSO_4$, 450."

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THE CHEMICAL NEWS.

VOL. CIX., No. 2848.

THE PREPARATION OF EYE-PRESERVING GLASS FOR SPECTACLES.*

By Sir WILLIAM CROOKES, O.M., F.R.S.

(Concluded from p. 291).

Glass 240.

FURTHER experiments with biotite showed that its special property was due to the iron protoxide it contained, and another glass was therefore made in which the iron could be introduced in the form of a definite salt of known composition. Ferrous oxalate was chosen, the proportions being as follows:—

Raw soda flux	90
Ferrous oxalate, $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$..	10

100

The glass made from this material does not cut off quite so much of the heat rays as the one prepared from biotite, the rays obstructed being 88 as against 94 per cent. But the ultra-violet is entirely intercepted, the limit being λ 3950. It transmits 36 per cent of the luminous rays. It is of a smoky green colour. The tintometer numbers are:—Yellow, 4.0; blue, 4.0.

Glass 246.

This is a glass made on a larger scale at the Whitefriars Glass Works, and of the same composition to start with as Glass 240, namely, 10 per cent of ferrous oxalate with raw soda flux. At the suggestion of Mr. Harry Powell a small quantity of red tartar and powdered wood charcoal was added to prevent oxidation; the resulting glass is sage-green in colour, a plate 2 mm. in thickness cuts off ultra-violet rays down to λ 3800, its opacity to heat radiation is 98 per cent, and it transmits 27.6 of the incident light. The tintometer numbers are:—Yellow, 5.5; blue, 11.0.

A plate of this glass 1 mm. thick cuts off the ultra-violet rays down to λ 3550, its opacity to heat radiation is 83 per cent, and it transmits 47.9 per cent of the incident light. The tintometer numbers are:—Yellow, 2.5; blue, 5.0.

Glass 247.

Raw soda flux	92.00
Cerium borate	6.30
Nickel oxide	0.04
Ferric oxide	1.60
Chromic oxide	0.06

100.00

Glass 247 has a faint green tint and is practically opaque to the ultra-violet rays, the limit being λ 3620. It obstructs 29 per cent of the heat radiation, and transmits 71 per cent of the luminous rays. The tintometer numbers are:—Yellow, 2.0; blue, 2.0.

Glass 248.

Fused soda flux	94.60
Cerium nitrate, crystallised ..	4.72
Uranic oxide	0.30
Nickel oxide	0.30
Cobalt sulphate, crystallised ..	0.08

100.00

Glass 248 is similar in composition to the one previously described (197), but is of a darker neutral tint. It is opaque

to ultra-violet rays shorter than λ 3550, and cuts off 47 per cent of the heat radiation. It transmits 30 per cent of the incident light. Its tintometer numbers are:—Red, 2.0; yellow, 2.5; blue, 7.5.

Glass 249.

Fused soda flux	88.47
Ferric oxide	1.50
Cobalt sulphate, crystallised ..	0.03
Cerium nitrate, crystallised ..	10.00

100.00

Glass 249 is of a pale blue tint almost opaque to the ultra-violet rays, the limit of wave-length being λ 3550; to all rays of shorter wave-length it is opaque. It cuts off 51 per cent of the heat radiation, and transmits 63 per cent of the luminous rays. Its tintometer numbers are:—Yellow, 0.5; blue, 2.0.

Glass 250.

Raw soda flux	88.00
Cerium borate	5.00
Ferrous sulphate, crystallised ..	4.15
Uranoso-uranic oxide	2.75
Chromic oxide	0.10

100.00

Glass 250 has a yellow colour with a faint tinge of green. It cuts off ultra violet light, being opaque to radiation shorter than λ 3685. It only obstructs 25 per cent of the heat rays, and is transparent to the extent of 74 per cent. In the tintometer the numbers are:—Yellow, 7.00; blue, 1.25.

Glass 251.

Raw soda flux	92.0
Ferrous sulphate, crystallised ..	8.0

100.00

During the fusion the iron is partially peroxidised. Glass 251 is of a faint yellow colour; it is opaque to ultra-violet rays shorter than λ 3550, it obstructs 37 per cent of the heat radiation, and it transmits 89 per cent of the incident light. Its tintometer number is:—Yellow, 1.25.

Glass 252.

Raw soda flux	72.60
Cerium nitrate, crystallised ..	24.00
Copper sulphate, crystallised ..	2.10
Nickel oxide	0.40

100.00

The colour of Glass 252 is faint bluish green. In it copper is introduced to counteract the yellow-brown tint given by the cerium and nickel, and to obtain a tint approaching neutral. It is opaque to ultra-violet rays of shorter wave length than λ 3680, cuts off 47 per cent of the heat radiation, and transmits 45 per cent of light. The tintometer numbers are:—Yellow, 2.0; blue, 4.5.

Glass 253.

I have already explained that black mica (biotite) is almost perfectly transparent to heat radiation, and at the same time opaque to the luminous rays. I thought it would be interesting to see what would be the effect of melting up some pieces of highly diathermanous biotite with soda flux. After many experiments it was found that a glass of a neutral tint could be made by melting biotite at a high temperature and fusing the result with flux. The proportions are—

Raw soda flux	88.5
Black biotite, fused	11.5

100.00

On testing the resulting glass it was found that it had remarkable properties in respect to the heat rays, but in exactly the opposite way to what was expected. It offers

* Read before the Royal Society, November 13, 1913. From the *Philosophical Transactions of the Royal Society*, Series A, vol. cxciv., pp. 1-25.

n almost complete obstruction to the invisible heat rays, and it cuts off 94 per cent of the heat radiation, and allows 30 per cent of the incident light to pass through. It is opaque to ultra-violet rays of shorter wave-length than λ 3610. It is of a sage-green colour, and its tintometer numbers are:—Yellow, 4.0; and blue, 7.0.

Discussion of the Foregoing Results.

I have already said that the progress of this research has widened since I commenced investigations three years ago. Then my object was to find a glass which would cut off the heat so as to preserve the eyes of those engaged in Glass works. I soon found it difficult, even if it were advisable, to confine the research to the action on heat rays alone. Thus the glasses now described include specimens suitable for spectacles adapted to all requirements—from Eyes of Youth to Eyes of Age.

The first necessity therefore is to find a glass which will cut off as much as possible of the heat radiation. Glass 246—sage-green in colour—is almost perfect in this respect, as it cuts off 98 per cent of the heat. Glass 217—of a pale blue tint—is opaque to 96 per cent of heat radiation. Next comes Glass 253—of a neutral tint—which cuts off 94 per cent; and then come Glass 240—of a neutral tint—cutting off 88 per cent, Glass 210—of a green tint—cutting off 87 per cent heat radiation, and Glass 158—of a pale greenish yellow—cutting off 63 per cent of the heat radiation. If more light is desired to enable the workers to see better at the expense of a little athermancy, Glass 249 is commendable. It is a very pale blue and transmits 63 per cent of luminous rays while cutting off 51 per cent of the heat rays. Spectacles of this glass scarcely appear to obstruct light at all, and the colours of objects are practically unchanged.

For ordinary use, when no special protection against heat radiation is needed, the choice will rest on whether the ultra-violet or the luminous are most to be guarded against; or whether the two together are to be toned down. To begin with I will take into consideration glasses most effective in cutting off ultra-violet rays. Ordinarily the visible spectrum is assumed to end at the Fraunhofer line K, λ 3933, but light can easily be distinguished some distance beyond by the naked eye. For instance, about fifty years ago, with a quartz spectroscope with solar rays, I could see L, λ 3820, and M, λ 3727, though now I cannot see above K. It may therefore be considered that the ultra-violet rays which are to be cut off on account of their probable injurious action are those of shorter wave-lengths than, say, λ 3700. The most effective glasses for this purpose are 158, 150, 240, 246, 202, and 197, all of which are opaque to rays shorter than 3700. The colours are pale green, yellow, and neutral; they transmit ample light so that a choice of tints is available to suit individual taste.

If much transparency is required there is a choice between glasses 187, 150, 251, 250, 247, and 238, which transmit from 99.5 to 70 per cent of the incident light. The choice between this range of glasses will depend on the conditions required, *i.e.*, on the absolute transparency or the colour. The colours are pale tint of yellow, green, and neutral.

If only a moderate degree of transparency is desired Glasses 158, 249, and 221 may be selected; the light transmitted ranges from 70 to 60 per cent, and the tints are of pleasant green, blue, and orange.

When glasses are required which are restful to the eyes in the glare of the sun on chalk cliffs, expanses of snow, or reflected from the sea, Glasses 249, 197, 252, 165, 210, and 248 are most suitable, the tints being yellow, green, and neutral. Moreover, they have the advantage of cutting off practically all the ultra-violet rays and also a considerable amount of the heat radiation.

For convenience of reference all the glasses above described are arranged in the following four tables:—

- I. Absorption of Heat Rays.
- II. Absorption of Ultra-violet Rays.
- III. Transmission of Luminous Rays.
- IV. Reduction of Glare.

This latter property is the most valuable for general use in brilliant light.

TABLE I.—Absorption of Heat Rays.

Glass No. 246 cuts off 98 per cent.			
"	217	"	96
"	253	"	94
"	240	"	88
"	210	"	87
"	158	"	63

TABLE II.—Absorption of Ultra-violet Rays.

Glass No. 240. Opaque to rays of, shorter w.l. than			
"	202	"	3830
"	246	"	3800
"	197	"	3800
"	158	"	3700
"	221	"	3685
"	150	"	3620

TABLE III.—Transmission of Luminous Rays.

Glass No. 187 transmits 99 per cent

"	251	"	89
"	250	"	74
"	150	"	73
"	247	"	71
"	238	"	71

TABLE IV.—Reduction of Glare.

Glass No.	Absorption of heat.	Absorption of ultra-violet.	Transmission of light.	Colour.
	Per cent.		Per cent.	
249	51	3550	63	Pale blue
197	41	3800	45	Pale neutral
252	47	3680	45	Faint blue-green
165	38	3680	42	Pale yellow-green
210	87	3620	30	Blue-green
248	47	3550	30	Dark neutral

THE COMPRESSION AND DENSITY OF RAW MATERIALS USED IN THE MANUFACTURE OF PAPER.

By CLAYTON BEADLE and HENRY P. STEVENS.

Wood, in point of quantity, is the chief source of raw material for the manufacture of paper. Certain countries, like Scandinavia, Russia, Finland, Germany, Canada, United States, are big pulp producing countries, and what they do not require for their own use they export. Other countries, such as Great Britain and parts of the British Empire other than Canada, France, Italy, Spain, Austria, China, and Japan, which are big paper making countries, depend on outside sources of supply of wood-pulp. As supplies for such countries come from long distances over the seas, freight is a matter of great importance. The freight is largely determined by bulk, and therefore the question of density, not only of bales of wood-pulp but also other forms of paper making raw materials, is of very great importance. There are several fibres that would be worth while considering as raw materials in the manufacture of paper if it were not for their excessive bulk, which would put such a freight upon them as to render the cost of delivery into this and other importing countries prohibitive, in spite of the fact that such materials may be had for the asking in the localities where they grow. Straw as raw material in the manufacture of pulp and paper has been killed in this way in England. Esparto, which is a somewhat bulky material, has the compensation of cheap back freight from the shores of the Mediterranean.

The question of bulk in the natural state of growth or gathering is of secondary importance, provided that a high

density by compression can be obtained at a reasonable cost. The object of this communication is to show what densities are commercially obtainable with a few of the paper making raw materials.

TABLE A.—Density Equivalents.

Cubic feet per ton.	Pounds per cubic foot.	Sp. gr. (water = 1.00).
23.8	93.7	1.500
25	89.6	1.433
30	74.7	1.195
35	64.0	1.024
40	56.0	0.896
45	49.6	0.796
50	44.8	0.717
60	37.3	0.597
70	32.0	0.512
80	28.0	0.448
90	24.9	0.398
100	22.4	0.358
110	20.4	0.326
120	18.7	0.300
130	17.2	0.275
140	16.0	0.256
150	15.0	0.240
200	11.2	0.179
250	9.0	0.143
300	7.5	0.120
350	6.4	0.102
400	5.6	0.090

Table A gives equivalents in cubic feet per ton and pounds per cubic feet, and density or specific gravity (water = 1.00). This table will be found useful for reference when considering the subject generally. As cellulose and vegetable fibres generally, as used or available for use in the manufacture of paper, possesses a specific gravity of 1.500, or a figure very closely approximating thereto, any cellulosic material compressed to its final condition so as to eliminate all air space would have a gravity of 1.500 and would weigh 93.7 lbs. to the cubic foot = 23.8 cubic feet per ton. This figure is inserted at the top of Table A in order to see how nearly highly compressed bales approach to the ultimate condition of compactness, and by the aid of such figures it is easy to calculate from any density obtained by hydraulic pressing the percentage by volume of air space and fibre. Compression of this order, *i.e.*, approaching the complete elimination of air space, is brought about when paper is highly compressed for coverings of calender bowls, or for structural work as for the interiors of railway waggon wheels; but this compression is never quite to the extent of eliminating the whole of the air space.

In practice, for the baling of raw material to be used in the manufacture of paper, the extent of compression is limited (a) by the cost of compression, (b) by the condition of the material when compressed, and (c) the question of deadweight. Heavy compression within limits can be brought about at a reasonable cost per ton, but the first cost of installation is greatly augmented if high compression is to be resorted to. High compression cannot be done cheaply unless operated on an extensive scale, and the hydraulic presses are heavy, but it is a comparatively easy thing to give a medium compression such as 20 to 25 lbs. per cubic foot, even by hand or horse labour and with comparatively inexpensive light and portable presses. Then, again, the compression must not be carried to the extent of destroying or damaging the paper making qualities of the raw material. High compression with some materials is very detrimental on account of the breaking up of the fibres during the compression. For instance, an excessively high density in the case of esparto would be destructive, and would make it very difficult to conduct the subsequent operations of opening up, dusting, &c., preparatory to boiling. There is a limitation here in the amount of compression, which is of necessity much less than in the case of chemical or mechanical wood pulp;

but with cotton-seed cotton, which is discharged direct from the bales into the boiler, high compression such as can be obtained by the most powerful hydraulic presses is, in our opinion, of no detriment provided that the material is sufficiently broken up to ensure the complete penetration and circulation of liquor during the process of boiling. The same may be said of *Hedychium coronarium*, and, as will be hereafter seen, this fibre is capable of very high compression without destroying or impairing its paper making qualities. Table A ranges from completely compressed cellulose materials to materials in a loose unbaled or piled up condition.

The third limitation point in regard to compression, namely, deadweight, must not be lost sight of. Since deadweight comes in at 40 cubic feet per ton (= 56 lbs. per cubic foot), there is no use compressing beyond this point unless it be, perhaps, for land transport and storage in warehouse and factory.

TABLE B.—Comparative Densities of Different Raw Materials used in the Manufactures of Paper.

	Cubic feet per ton.	Pounds per cubic foot.
Esparto bales	120	18.7
Do. Hydraulic press	90	24.9
Moist "mechanical" wood-pulp (50 per cent water	44	51
Do. Mean	36	61
Do. Equivalent dry weight	40	56
Moist "mechanical" wood-pulp (50 per cent water	80	28
Do. Equivalent dry weight	40/45	56/50
Chemical wood-pulp (sulphite), ordinary compression, air dry	80/90	28/25
Best practice for sulphite, air dry	65	34
Chemical wood (soda) kraft, dry	50	45
Chemical wood-pulp (sulphite), dry by measurement and weight of bales in mills	80	28
Do. Mean	61.6	36.4
Hedychium coronarium, continuous light baling press	54	41.5
Do. "Heavy"	57.8	39
Do. Heavy hydraulic presses	90	25
Do. Greatest compression obtained with bales (dry)	64/56	35/40
Do. (Wet)	37/38	60/61
	33/34	66.0
	33/34	66.8

Table B shows a comparison of densities of different paper making materials. It will be noticed that the bulk'est material is esparto. Moist mechanical wood-pulp reaches deadweight, but inasmuch as it contains 50 per cent of water a dry ton has a volume of 80 to 90 cubic feet. Serious attempts have been made in modern pulp mills to compress to 40 per cent of moisture, but it is doubtful whether this will be accomplished economically. There appears to be a greater uniformity of compression in the case of "mechanical" than with "chemical" wood-pulp. This may be due to the fact that in the case of mechanical a definite amount of moisture is aimed at, namely, 50 per cent, and this is regulated by the amount of compression. There is also the important difference that mechanical is pressed moist and chemical compressed dry. "Soda" or sulphate pulp, as might be expected, gives less compression than sulphite; the sheets of sulphite are made compact before baling, but the amount of compression, whether for chemical or mechanical, varies with different mills, according to the power installation and the qualities of the pulp-wood as well as the wood-pulp operated upon. There is a great difference in the qualities of "sulphite" and "soda," one being much harder than the other, and mechanical varies very much in its qualities according to the sources of supply, the mode of grinding, and so forth. The mean results for moist mechanical, taken by us from different sources, show practically the same figures, *i.e.*, 40 cubic feet per moist ton = 56 moist pounds per cubic foot, which

is deadweight. The first figures given for moist mechanical show how the density varies between individual bales, the second figures were arrived at from measurements made in bulk.

Hedychium baling was tested first of all in continuous light baling presses. The *Hedychium* operated upon was in the condition as shipped from Brazil, i.e., after passing through crushing rolls and drying prior to shipping, that is in the form of a loose tow. *Hedychium* as piled or packed loose has a density of about 5 lbs. to the cubic foot. On packing into digesters it will occupy about 10 lbs. per cubic foot. With Howard's Dreadnought heavy continuous presses it gives bales of a density of from 35 to 40 lbs. per cubic foot; with lighter presses of the same type 25 to 30 lbs. per cubic foot. Either the light continuous or heavy Dreadnought presses will bale material at the rate of 20 tons dry weight per diem. For greater densities it is advisable to employ hydraulic pressure. With heavy compressions with hydraulic presses 60 lbs. per cubic foot is obtainable, which is more than is necessary for deadweight. In order to see what was the greatest density obtained with *Hedychium*, pressures of over 1 ton per square inch were employed on small bales at the works of Messrs. Howard and Sons. The highest compression for dry *Hedychium* in the form of bales was 66 dry lbs. per cubic foot. This compression is not detrimental to the qualities of the product. In this condition of baling it can be used for the manufacture of paper, and without these qualities having been impaired as the result of high compression. For moist *Hedychium* we obtained bales containing 66.8 moist lbs. per cubic foot.

TABLE C.—Laboratory Baling Tests with *Hedychium*.

	Grms. per cc.	Lbs. per cub. ft.
Raw dry <i>Hedychium</i> , pressed in Cider Press—		
Packed before pressing	0.089	4.4
Do. Whilst under pressure	0.355	17.6
Boiled <i>Hedychium</i> , pressed in Cider Press—		
Gross weight (68 per cent moisture) ..	1.20	75.0
Equivalent dry weight	0.385	24.0
Baling in iron cylinder—		
Raw dry, under pressure	1.24	77.5
Do. Pressure released	1.00	62.5
Raw wet (47 per cent moisture), under pressure. Dry weight	1.00	62.5
Do. Pressure released. Dry weight ..	0.71	44.4
Ordinary pressing without a "former"—		
Gross weight (55 per cent moisture) ..	1.00	62.5
Equivalent dry weight	0.45	28.2
Gross weight (42 per cent moisture) ..	1.20	75.0
Equivalent dry weight	0.695	43.5

Table C gives some experimental baling with *Hedychium* where the density is expressed in grms. per cc. and lbs. per cubic foot. This gives one some idea of the amount of diminution of volume during the process of baling. In practice the reduction in volume is considerable, one ton dry weight uncompressed occupying over 400 cubic feet, after compression less than 40, that is it reduces to about one-tenth. A continuous baling press, by producing bales of a density of 25–30 lbs. to the cubic foot, is well adapted to this work as a first operation. The next operation is best done by compressing two bales into one to a density of 60 lbs. to the cubic foot prior to shipment. The laboratory results obtained with cider presses in light compressions seem to indicate that greater dry weight per cubic foot can be obtained if the material is compressed in a moist rather than a dry condition. This is due to the material becoming more yielding to the pressure when moist than when dry, but when heavier pressures are employed the moisture taken up by the fibre causes it to swell somewhat and to offer a barrier to anything like complete compression, so that the reverse is the case,

namely, for high densities the dry goes closer than the moist. Thus 77 lbs. per cubic foot, before releasing from the presses, has been actually obtained in making dry compressions; this expands to 62 lbs. to the cubic foot when the pressure is released, but when the moist material, containing about its own weight of water, is similarly treated in iron cylinders, the density under full compression is 66 and when released 44 dry lbs. per cubic foot. The same is to be noticed when baling under hydraulic pressure recorded in Table R. In the case of the hydraulic pressed bales we obtained 66.0 dry lbs. from the dry pressing and 66.8 moist lbs. per cubic foot from the moist materials after release from press. Unfortunately we did not take note at the time of the dry weight in the wet baling, but we have since dried out the bale and find that it had a density of 38 dry lbs. per cubic foot under equal pressure with the former.

The conclusion is, therefore, that for moderate pressures and density, a greater dry weight per cubic foot is to be obtained baling moist than when baling dry, but that with hydraulic pressure for high densities, i.e., in the neighbourhood of dead weight, the greater dry density is obtained by baling air dry or in the neighbourhood of air dryness.

THE SCIENTIFIC WEEK.

From Our Own Paris Correspondent).

TREATMENT OF MALIGNANT TUMOURS BY THE X-RAYS.

As is well known the X-rays are now often employed in the treatment of superficial cancerous affections. Concerning this subject a very interesting observation has been made by MM. Reboul and Nogier, and communicated to the Academy of Sciences by M. Roux, director of the Pasteur Institute. These authors have observed that when the X-rays are employed in successive applications in the treatment of malignant tumours, in certain cases the action of these rays grows gradually weaker, and that at a certain moment cancerous elements are no longer reached and affected by the treatment, before a complete cure has been obtained. These decreases of the radiosensibility appear to result from a kind of habit; that is to say, that the cancerous elements grow used to the X-rays, whose effect is thus lessened. The case is not always the same in all the subjects nor in all the cases treated. In order to avoid these inconveniences, MM. Reboul and Nogier advise, whenever the action of the X-rays does not seem to be constant, to take away all that is possible of the tumour before beginning a fresh application of the rays.

MECHANISM OF THE INACTIVATION OF SERUMS BY DIALYSIS.

In a new technical notice by M. Tissot, communicated to the Academy by Prof. d'Arsonval, the author explains the conditions that govern the dissociation of soaps in serum as well as the mechanism of the inactivation of serums by dialysis, in view of establishing the nature and the constitution of the body that possesses the bacteriological power, that is to say "alexine."

DIFFERENT SPECIES OF LEAD.

The interesting hypothesis of the existence of several species of lead results from the researches of M. Maurice Curie concerning the atomic weight of lead of diverse origins. It is known that the radio-active theories, according to which certain bodies, such as radium, uranium, thorium, can evolve and become transformed into other elements, have had a striking confirmation by the transmutation of radium into helium. It is also known that

the same theories lead to the assigning as the ultimate term of the series of these transformations one of the most common metals, that is to say, lead, which thus is derived from the metal that at the present time is by far the dearest (several hundreds of thousand francs a grm.). Continuing his researches undertaken in this direction, M. Maurice Curie, for the atomic weight of lead existing in uraniferous ores, has found the figure of 206.5, whilst the atomic weight of ordinary or galenic lead is 207.01. From this he concludes that there are several varieties of lead of different atomic weights according to the initial metal from which they are derived.

ELECTION OF A PERPETUAL SECRETARY AT THE ACADEMY OF SCIENCES.

After a ballot in which 50 members voted, the Academy of Sciences has just elected, by 39 votes, M. Alfred Lacroix, Professor of Mineralogy at the Natural History Museum, as perpetual secretary for physical sciences, in place of the late M. Van Tieghem. The scientific works of M. Alfred Lacroix concern the mineralogy, geology, and physics of the globe. He has studied mineralogy quite as much as a naturalist and as a physicist. In the numerous papers he has published he has especially tried to seek out the mode of the formation of rocks and minerals and their rôle in nature, for he does not consider them as simple chemical salts. Instead of working in a laboratory he prefers to pursue his studies on the spot, in the most diverse regions of the world, employing experimentation whenever this was possible. Throughout all the scientific researches of Prof. Lacroix the same general directing idea, the same plan is to be found. When he studies the determination of properties, and in particular of the optical properties of minerals, he searches what are their variations, with the conditions of their layers and their mode of formation. He applies the data thus obtained to the determination of the composition of rocks and searches the origin of metamorphic rocks and those of the eruptive rocks which have produced them. His "Mineralogy of France and Her Colonies," his memoirs on metamorphism, his observations on the eruptions of Martinique, of Vesuvius, of Etna, of the volcanos of the Réunion are the principal steps of his scientific researches. Born at Macon in 1863, M. Lacroix was appointed assistant at the Collège de France in 1887, Doctor of Science in 1889, Professor of Mineralogy at the Natural History Museum in 1893; he became a member of the Academy of Sciences in 1904. He is a member of most of the different foreign scientific academies throughout the world, and has been charged with no less than fourteen scientific missions in nearly all the countries of the globe. As head of the mission of Mont Pelée in 1902, Prof. Lacroix created the Martinique Observatory, where he made some very fine researches on the eruptions of Mont Pelée. He contributed fresh information as to the formation of the domes raised by volcanic rocks, and also concerning a little known phenomenon, that of "*nuées ardentes*." These clouds of *nuées* were veritable agents of destruction and death, which clasped the eruption of Mont Pelée among the most homicidal that history has ever had to enregister. M. Lacroix was able to study, near at hand, seventeen eruptions of these thick clouds. He has seen them roll like a liquid on the surface of the soil. Their temperature at a distance of 6 kilometres from their point of departure was 200°. At this same time, the eminent mineralogist studied the volcano of Saint-Vincent and the sulphur mine of Guadeloupe. Lastly, the geological study that he has made of the large African island of Madagascar is one of the most important works of Prof. Lacroix.

King's College. - Professor Herbert Jackson, of King's College, has been appointed Head of the Chemical Department of the College, with the title of Daniell Professor of Chemistry in the University of London.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 4, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President,
in the Chair.

THE PRESIDENT referred to the loss sustained by the Society through the death of Sir Joseph Wilson Swan (elected, June 3, 1865; died, May 27, 1914).

Mr. D. R. Keller was formally admitted a Fellow of the Chemical Society.

A certificate was read for the first time in favour of Mr. George von Kaufmann, jun., Christ's College, Cambridge.

Of the following papers, those marked * were read:—

*153. "*The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus.*" By JAMES KENNER. (This paper was read at the meeting on May 21, 1914).

The influence mentioned in the title was referred to two distinct functions exercised by nitro-groups. One of these, which is shared with other meta-directive groupings, consists in the conferment of a certain degree of mobility on substituents in ortho- or para-positions, and was explained in terms of Flürscheim's views. The other enables the substituent, thus rendered mobile, to take part in reactions, in spite of the steric influences to which it is exposed. This function is exercised most powerfully by the nitro-group, and was correlated with another property characteristic of nitro-groups, namely, the power to form additive compounds.

An alternative theory, proposed by Borsche (*Annalen*, 1911, ccclxxvi., 356; 1913, cdii., 81) was also discussed.

With the assistance of Mr. R. Curtis, and in connection with the views developed above, the action of hydrazine hydrate on methyl 2-chloro-3:5-dinitrobenzoate was studied and shown to lead at once to the formation of 5:7-dinitro-3-keto-1:3-dihydroindazole, without admitting of the isolation of the intermediate hydrazine derivative. In the case of phenylhydrazine, the main product was 5:7-dinitro-3-keto-2-phenyl-1:3-dihydroindazole, accompanied by a small proportion of 2:4-dinitro-6-carbomethoxyhydrabenzene, and another compound of unknown constitution.

The indazole derivatives named gave rise to quinonoid sodium salts, whilst, by the action of phosphoryl chloride at 180°, 3:5:7-trichloroindazole and 3:5:7-trichloro-2-phenylindazole were produced, the nitro-groups attached to the benzene nucleus having suffered displacement by chlorine atoms.

DISCUSSION.

Dr. FLÜRSCHHEIM welcomed Dr. Kenner's paper as an interesting contribution on the problem of benzene substitution. It appeared that, generally, chemical reactivity was governed by the nature of the affinity of the atoms involved (polar factor), by the amount of that affinity (quantitative factor), and by considerations of space (steric factor). Dr. Kenner had taken the last two factors into consideration, and he had been able to embrace a considerable number of facts. At the same time the polar factor could, of course, not always be neglected. For the mobility, for instance, of a nitro-group in 1:3:5-trinitrobenzene (Lobry de Bruyn), of fluorine in *m*-fluoronitrobenzene (Holleman), or of the 1-bromine in 1:2:4:6-tetrabromobenzene (Jackson and Calvert), it even appeared that the polar factor was alone responsible; in other words, even when a sufficient amount of affinity was available for it, a substituent might easily be detached from the nucleus when both exhibited strong electropolarity of the same kind, so that the nature of their affinity was not conducive to mutual saturation (compare *Ber.*, 1906, xxxix., 2016). Undoubtedly, the problem of the replacement of one

benzene substituent by another was more complex than that of the mere substitution of hydrogen, and he was glad that Dr. Kenner had brought the subject before the meeting.

Prof. J. T. HEWITT referred to the work of Borsche and Bahr (*Annalen*, 1913, cdii., 81), which shows that in the apparently symmetrical 4:6 dichloro-1:3-dinitrobenzene, one halogen atom is more mobile than the other. This might be explained if the products with amines, &c., assumed a quinonoid configuration; for if the 6 chlorine atom had reacted, and quinonoid structure were established between positions 6 and 1, the linking between the carbon atoms 3 and 4 must of necessity be a single one.

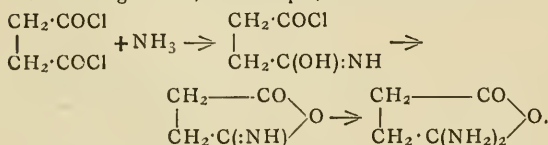
Dr. KENNER agreed that his views might need amplification in order to become applicable to all the observed cases of mobility, and cited, as an example, the formation of the trichloroindazoles mentioned above. In his opinion, recent work on the metallic ketyls lent strong support to the view that colour was connected with the presence of residual affinity, and therefore to Hantzsch's formula for the nitro-anilines. He drew attention to another apparent fallacy in the views expressed by Borsche and Bahr, and suggested an alternative explanation of the results obtained by these workers.

*154. "*Studies in the Succinic Acid Series. Part I. The Chlorides of Succinic and Methylsuccinic Acids, and their Constitution.*" By GEORGE FRANCIS MORRELL.

Since succinyl chloride gave with ammonia a 90 per cent yield of *as*-succinamide, and with benzene and aluminium chloride a similar amount of succinophenone, Auger (*Ann. Chim. Phys.*, 1891, [4], xxii., 326) concluded that it was a mixture of two isomerides. Meyer and Marx (*Ber.*, 1908, xli., 2459) found that it gave with alcohols only the normal esters, and suggested a theory of tautomerism. In the present investigation, succinyl and methylsuccinyl chlorides have been prepared, and a consideration of their physical properties and anomalous behaviour with ammonia and substituted ammonias is held to disprove Auger's theory, and to lend no support to the tautomerism theory. Succinyl chloride, for example, was found to be a crystalline solid, melting sharply at +20°, and boiling at 87–88°/18 mm. Whether the first or last portions of the distillate were taken, it gave with aniline nothing but the *s*-anilide (m. p. 230°); with methylamine, only a 15 per cent yield of the *s*-dimethylamide; and with ammonia almost entirely the *as*-amide.

It is concluded that these acid chlorides are definite chemical individuals, and that there is no satisfactory evidence whatever for assigning to them any other constitution than that of normal acid chlorides, $\text{COCl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COCl}$.

The formation of asymmetric products probably takes the following course, for example, with ammonia:—



*155. "*The Dilution Limits of Inflammability of Gaseous Mixtures. Part I. The Determination of Dilution Limits. Part II. The Lower Limits for Hydrogen, Methane, and Carbon Monoxide in Air.*" By HUBERT FRANK COWARD and FRANK BRINSLEY.

The smallest amount of hydrogen in an inflammable mixture of hydrogen and air has been variously stated as low as 4.5 and as high as 10 per cent. Similarly, the values given for the greatest amount of hydrogen in an inflammable mixture of hydrogen and air are as low as 55 per cent and as high as 80 per cent. The hydrogen-oxygen mixtures show similar want of accord in the results of previous workers. A partial explanation exists in Clowes's observation that in certain weak mixtures a flame may be propagated upwards, but not downwards.

A re-examination of the inflammability of weak gaseous mixtures has been started, based on the definition that a mixture at a defined temperature and pressure is inflammable *per se* if, and only if, it will propagate flame indefinitely, the temperature and pressure of the unburnt gases being constant. The flame observed in many weak mixtures travels more slowly than the convection current set up by the flame, so that the criterion of inflammability is the observed travel of a flame upwards through a vertical vessel of sufficiently great dimensions to avoid appreciable cooling influence by the walls and to provide a sufficient length for observation of the flame to leave no doubt as to its capacity for indefinite self-propagation.

The experiments of previous observers do not satisfy this criterion, and the critical experiments of the authors have been carried out in vessels, one having a capacity of 170 litres, another a length of 4.5 metres. With all three gases used, the flames in certain weak mixtures have been observed to start as vortex rings, which rose, expanded, and ultimately broke into a general self-propagating inflammation, or were extinguished. The lower limits of inflammability of mixtures of each of the three gases with air saturated with aqueous vapour at 17° to 18° were:—

Hydrogen	4.1 per cent
Methane	5.3 "
Carbon monoxide	12.5 "

DISCUSSION.

Prof. BONE drew attention to the great importance of accurate information concerning the behaviour of gaseous mixtures at or near the lower explosion limits, and congratulated the authors on both their experimental demonstration and the beautiful photographs which they had exhibited. He agreed in principle with the authors' definition of "inflammability," but pointed out the necessity of distinguishing between "ignitability" and inflammability. The phenomenon of ignition was very complicated, and was probably not a purely thermal one, as Prof. W. M. Thornton had recently shown in an important communication to the Royal Society on the electrical ignition of gaseous mixtures, from which it appeared probable that ionisation was a factor precedent to the actual combustion.

Dr. SCOTT suggested that the mixtures of hydrogen with oxygen and with air might be made more luminous by using weighed quantities of sodium, which would give the required quantities of hydrogen in contact with the water. The brilliant yellow of the flame would probably enable much more detail to be visible to the eye and to be recorded on the photographic plate.

Dr. E. RIDEAL asked whether there was any indication of a dark wave preceding the luminous cap which travelled up the tube.

The dark wave caused by local compression of the gas could be conveniently photographed by a method which he had used with great success in the case of rifle bullets travelling through different gases. The bullet in its course is made to traverse two copper gauze disks placed close to one another; by this means contact is made between the two disks, which are connected to the outsides of the Leyden jars of a Wimshurst machine. The primary spark follows a short time after contact is made, and if there is a photographic plate opposite to the spark-gap of the Wimshurst, the bullet, passing between the spark and the plate, throws its shadow on the latter. In front of the photograph of the bullet is always observable a parabolic-like curve, being a cross-section of the paraboloid-shaped mass of compressed air partly dragged and partly pushed forward by the bullet in its flight. The line on the plate is caused by the fact that the compressed air has a different refractive index to that surrounding it. Different gases gave curves of the same order, but different constants. In the present case, during combustion one might expect local differences of pressure, indications of which could be obtained by an adaptation of the foregoing method.

Dr. COWARD agreed with Prof. Bone that it was desir-

able to distinguish between inflammability and ignitability. A large flame might be developed in a mixture when an electric spark was passed or a jet of flame introduced into it, although the inflammation would not be capable of indefinite self-propagation. This mixture would therefore not be inflammable *per se*, but a possibly dangerous flame might be formed in it; the initial impetus of the spark was not rapidly dissipated. The authors had seen such flames in mixtures just below the dilution limit which were nearly 30 cm. wide, and travelled 60, 90, or even 120 cm. from their source.

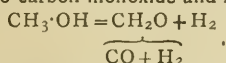
Dr. Scott's suggestion for rendering the hydrogen flames more luminous would be useful for photographic purposes; up to the present, the authors had desired to see and record the appearance of flame in pure mixtures, and for that reason to avoid the presence of spray or dust particles.

*156. "The Thermal Decomposition of Methyl Alcohol." By WILLIAM ARTHUR BONE and HAMILTON DAVIES.

The authors find that methyl alcohol vapour decomposes on heating principally in two ways, namely:—

1. An essentially low-temperature decomposition into, primarily, steam and a residue, CH_2 , which has a fugitive free existence, $\text{CH}_3\cdot\text{OH} = \text{CH}_2 + \text{H}_2\text{O}$.

2. The normal high-temperature decomposition primarily into formaldehyde and hydrogen, the formaldehyde then decomposing into carbon monoxide and hydrogen,—



Thus, at 650° , 20 to 25 per cent of the methyl alcohol decomposes according to (1), the remainder according to (2), the H_2C : formed during (1) combining with part of the H_2 produced during (2), forming methane.

At 1000° , more than 95 per cent of the methyl alcohol decomposes according to (2), the remainder according to (1).

At neither temperature is there any separation of carbon, nor could any acetylene be detected in the products.

157. "A Comparative Study of the Absorption Spectra of some Compounds of Phosphorus, Arsenic, Antimony, and Bismuth." (Preliminary Note). By CECIL REGINALD CRYMBLE.

In accordance with the rule connecting valency and absorption (*Trans.*, 1912, ci., 266), it has been found that solutions of compounds of the above elements absorb ultra-violet light, the extent of the absorption varying greatly with the nature of the compound.

If the chlorides ECl_3 are compared, the limit of general absorption is displaced towards the visible on passing from phosphorus chloride to bismuth trichloride, and in the latter compound an absorption band makes its appearance in Bi/1000 solution with a head at 2850 .

The pentachlorides of phosphorus and antimony have been examined, and they possess much greater absorptive power than the corresponding trichlorides. The limit of the general absorption of antimony trichloride and the absorption band of bismuth chloride are displaced towards the visible on formation of the complex salts $\text{ECl}_3\cdot n\text{MCl}$.

Like sulphates and selenates, the highly oxidised phosphates and arsenates are quite diatinctic; antimonates and arsenites show slight absorption; and, as is known, bismuthic acid is a red powder.

The grouping P:O in the phosphorus oxy-acids is devoid of absorptive power, and phosphoryl chloride is almost diatinctic.

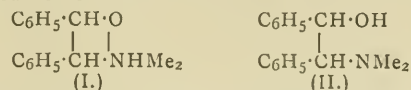
The investigations are being extended to the fourth group of elements, especially to tin and lead; and from the variations in the absorptive power of solutions of stannic chloride, which occur on keeping, it is hoped to gain some information on the constitution of these salts.

158. "The Reactions of α -Amino- β -hydroxy-compounds as Cyclic Structures." By JAMES COLQUHOUN IRVINE and ALEXANDER WALKER FYFE.

The behaviour of β -hydroxy- α - β -diphenylethylamine to-

wards methylating agents has been studied in order to ascertain if compounds in which a secondary hydroxyl group and a primary amino-group are attached to neighbouring carbon atoms are capable of reacting in accordance with a cyclic formula. By the action of silver oxide and methyl iodide on the amine, a dimethyl derivative melting at 135 — 137° was obtained. As this compound contained no normal methoxyl group, yet nevertheless failed to form a methiodide, a hydrochloride, or a platinichloride, it is regarded as the anhydride of β -hydroxy- α - β -diphenylethyl-dimethylammonium hydroxide (I.). In the absence of salt forming properties, and in its capacity to combine with silver iodide, the compound resembles the alkyl glucosamines, for which a cyclic structure has already been suggested.

On the other hand, direct methylation of β -hydroxy- α - β -diphenylethylamine by means of methyl iodide gave successively β -hydroxy- α - β -diphenylethylmethylamine, β -hydroxy- α - β -diphenylethylmethylamine (II.), and the corresponding methiodide. The properties of these substituted amines are perfectly regular in that they form salts and platinichlorides, from which it may be concluded that the normal open-chain structure may be applied to them. The following formulæ are consequently ascribed to the isomeric compounds isolated:—



The constitution assigned to β -hydroxy- α - β -diphenylethylmethylamine (II.) was confirmed by the conversion of the compound into β -methoxy- α - β -diphenylethylmethylamine, $\text{OMe}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{NMe}_2$, which, in turn, reacted with nitrous acid to give hydrobenzoin methyl ether. The same methoxy-amine resulted from the methylation of β -methoxy- α - β -diphenylethylamine, both by the silver oxide reaction and by the agency of methyl iodide, the compound in the former case being isolated as the methiodide combined with one molecule of silver iodide.

The results of the investigation are applied to the constitution of the alkyl glucosamines, and the capacity of these compounds to combine simultaneously with alkyl haloids and with silver haloids is explained on the assumption that the addition takes place through the oxygen atom of the ring.

159. "Ionic Equilibria Across Semi-permeable Membranes." By FREDERICK GEORGE DONNAN and ARTHUR JOHN ALLMAND.

Experiments have been made on the distribution of potassium chloride between two compartments separated by a copper ferrocyanide membrane, one compartment containing potassium ferrocyanide. The higher concentration of potassium chloride in the solution free from ferrocyanide, and the quantitative relation of this unequal distribution to the concentration of chloride and ferrocyanide, have been established.

The results agree, in general, with the view of such membrane-equilibria proposed by Donnan. A discussion of the distribution data and the measurements of electromotive force appears to show that, at all events in the case of a copper ferrocyanide membrane and potassium ferrocyanide solutions, the phenomena are quantitatively not so simple as supposed in the theory mentioned.

160. "The Effect of Ring-formation on Viscosity." By FERDINAND BERNARD THOLE.

The opinion previously put forward that ring-formation is accompanied by an increase in viscosity has been confirmed by a comparison of the viscosities of a considerable number of cyclic compounds (carbocyclic and heterocyclic rings containing from two to seven atoms) with those of corresponding open-chain analogues. The chemical types of the latter have been carefully chosen to correspond with those of the cyclic compounds, since the results of some previous investigators with other physical properties have been confused by illegitimate comparisons.

Viscosity has been found to fall in line with certain other physical properties in showing an anomaly which varies steadily as the complexity of the ring increases, and giving no change of direction on passing the five-membered ring-system.

161. "Action of Monochloroacetic Acid on Thiocarbamide and Monoalkylated Thiocarbamides." By PRAFULLA CHANDRA RAY and FRANCIS V. FERNANDES.

By the action of monochloroacetic acid on thiocarbamide in aqueous solution, the latter evidently tautomerises, and gives rise to formamidinethiolactic acid, $\text{NH}_2\text{C}(\text{NH})\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. If, however, acetone is used as a solvent, the corresponding hydrochloride of the base is obtained. Similar hydrochlorides are yielded by the action of monochloroacetic acid on mono-substituted thiocarbamides in acetone solution; thus, the hydrochlorides of methylformamidine- and allylformamidine-thiolactic acids have been prepared.

162. "Action of Grignard Reagents on Acid Amides." By ALEX. MCKENZIE GEOFFREY MARTIN, and HAROLD GORDON RULE.

In continuation of former work (McKenzie and Wren, *Trans.*, 1908, xciii., 310; xcvi., 473; Wren, *Trans.*, 1909, xcv., 1583, 1593), the authors have examined the action of Grignard reagents on several acid amides. In those cases where a ketol was isolated as one of the products, the yield was small. A mixture of benzoin and $\alpha\beta$ -dihydroxy- $\alpha\beta$ -triphenylethane is produced by the action of magnesium phenyl bromide on mandelopiperidide. The formation of benzoylbenzylcarbinol from α -hydroxy- β -phenylpropionamide is accompanied by the formation of $\alpha\beta$ -dihydroxy- $\alpha\gamma$ -triphenylpropane.

d-Benzoylbenzylcarbinol undergoes racemisation at the ordinary temperature when a few drops of sodium ethoxide are added to its alcoholic solution. This change is, however, much slower than that undergone by *l*-benzoin under similar conditions; the value for the rotation of a 5 per cent solution falls to about one-half of the original after 481 hours have elapsed.

163. "Synthetic Hydrocarbons Allied to the Terpenes." By WALTER NORMAN HAWORTH and ALEXANDER WALKER FYFE.

The method used by Blaise (*Comptes Rendus*, 1901, cxxxi., 1217) for the production of ketones from nitriles has been applied in the synthesis of three hydroaromatic ketones of the cyclohexene series. These were converted into optically active and inactive carbinols and hydrocarbons analogous to the members of the terpene group. The alteration in the rotation values due to the synthetic changes has been carefully studied, as have also the spectrochemical properties. The compounds described are interesting examples of "multiple disturbance" of conjugation, and show the expected diminution of exaltation in accordance with the views of Auwers and Eisenlohr.

164. "Asymmetric Tervalent Nitrogen." (Preliminary Note). By TOM SIDNEY MOORE.

The cause of the failure of the attempts that have been made to obtain optically active compounds owing their asymmetry to the presence of trivalent nitrogen atoms attached to three different groups is probably the rapid racemisation of the substances investigated, which have

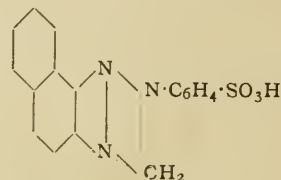
all been of the type $\text{N} \begin{smallmatrix} a \\ \diagdown \\ b \\ \diagup \\ c \end{smallmatrix}$.

Compounds of the type $\text{N} \begin{smallmatrix} a \\ \diagdown \\ b \\ \diagup \\ c \end{smallmatrix}$ and $\text{N} \begin{smallmatrix} a \\ \diagdown \\ b \\ \diagup \\ b \end{smallmatrix}$, in

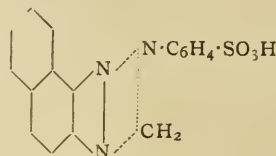
which *a*, *b*, and *c* are three different divalent groups or chains, of which at least one is unsymmetrical with regard to the two nitrogen atoms, should exist in two enantiomorphic forms. Racemisation might be expected to be slow, or even non-existent, in compounds of the first type, and it might be slow enough in compounds of the second type to allow of the demonstration of isomerism. Ex-

periments on the preparation of suitable compounds of the first type are now in progress; of the second type several examples are known, and one of these has been examined.

The compound chosen was 2-*p*-sulphophenyl-2 : 3-dihydro-1 : 2 : 4-naphthaisotriazine, which was prepared according to the general method given by Meldola and Forster (*Trans.*, 1891, lix., 678), and found to be very similar in properties to the phenyl derivatives described by them. The two possible forms would be:—



and—



The following results were obtained with a specimen of the brucine salt of this compound after it had been twice re-crystallised from alcohol:—

1. The brucine salt was treated at 0° with excess of *N*-sodium hydroxide, and the resulting aqueous solution extracted with chloroform until it was free from brucine (three extractions). In four such experiments the resulting alkaline solution of the sodium salt showed a small but definite dextrorotation, which decayed with time, until after a few hours the solution was optically inactive. The values for the initial specific rotation of the sodium salt were between + [3.5°] and + [1.7°]. Parallel experiments with the acid itself gave, as one expected, inactive solutions. In other experiments with the brucine salt, where only the equivalent quantity of sodium hydroxide was used, the solution of the sodium salt was inactive; this agrees with the experience of Mills and Bain (*Trans.*, 1910, xcvi., 1866; 1914, cv., 64), who found that excess of alkali hindered the racemisation of their compounds.

2. The brucine salt, when added to chloroform, first dissolves completely, and then deposits some of the acid, this process not being complete for some hours. One such solution was allowed to remain overnight, and its rotatory power was measured after filtration. It was then kept for three days in a closed vessel (during which period no further acid was deposited), and its rotatory power again measured. The angles observed were -0.15° and -0.22° respectively. This change of rotatory power with time indicates that the brucine salt contained an excess of the dextro-acid, which racemised gradually on keeping.

Mr. J. J. Manley very kindly estimated the sulphur in a specimen of the acid recovered from the brucine salt.

Found, S = 9.65. $\text{C}_{17}\text{H}_{13}\text{O}_3\text{N}_3\text{S}$ requires S = 9.44 per cent.

The author is proceeding with a detailed examination of this and similar compounds; in the meantime, the results given above offer definite evidence of asymmetry in trivalent nitrogen atoms attached to three separate groups.

165. "The Alkaloids of *Daphnandra micrantha*." By FRANK LEE PYMAN.

The alkaloids of the bark of the Queensland plant, *Daphnandra micrantha*, Benth., have been investigated, and three new crystalline bases, *daphnandrine*, $\text{C}_{36}\text{H}_{38}\text{O}_6\text{N}_2$, *daphnoline*, $\text{C}_{34}\text{H}_{34}\text{O}_6\text{N}_2$ (or $\text{C}_{35}\text{H}_{36}\text{O}_6\text{N}_2$), and *micranthine*, $\text{C}_{36}\text{H}_{32}\text{O}_6\text{N}_2$, have been isolated and characterised.

166. "The Relation between the Absorption Spectra and the Constitution of certain isoquinoline Alkaloids and of the Alkaloids of *Ipecacuanha*." By JAMES JOHNSTON DOBBIE and JOHN JACOB FOX.

It was shown that certain isoquinoline alkaloids including tetrahydroberberine, laudanose, corydaline, the salts of cryptopine and protopine, which possess similar spectra, are all characterised by the presence of unreduced nuclei derived from catechol. When the spectra of one molecule of these alkaloids are compared with the spectra of two molecules of creosol (4-hydroxy-3-methoxytoluene), they are seen to have their band in the same position. In these, as in cases previously described (*Trans.*, 1911, xcix., 1254; 1912, ci., 77; 1913, ciii., 1193), the reduced part of the molecule has very little influence on the spectrum.

It was also shown that the band of the spectrum of morphine, which contains one catechol nucleus, only differs from that of creosol in being somewhat narrower.

Emetine and cephaeline give the same spectrum as the above-mentioned alkaloids, and therefore in all probability also contain catechol nuclei, a conclusion which is in harmony with the facts of their constitution, so far as these are known (Carr and Pyman, *Proc.*, 1913, xxix., 226; 1914, xxx., 157).

167. "The Interaction of Benzoin and the Chlorides of Dibasic Acids." By HAMILTON MCCOMBIE and OHN WILFRID PARKES.

The interaction of benzoin and dibasic acid chlorides was studied in the hope of obtaining compounds derived from one molecule of benzoin and one molecule of the acid chloride, which would prove to be derivatives of stilbenediol. The following acid chlorides were employed:—Carbonyl chloride, oxalyl chloride, phthalyl chloride, and camphoryl chloride. In all cases, however, even when excess of benzoin was employed, the only compounds that could be isolated were formed from two molecular proportions of benzoin and one of the acid chloride. In the case of oxalyl chloride, two different compounds were isolated, both possessing the formula $C_{30}H_{22}O_6$.

168. "The Fractional Distillation of Petroleum." By JAMES MCCONNELL SANDERS.

In the examination of crude petroleum, burning oil, or petrol by the distillation test, it is often desirable to determine the specific gravity of successive fractions; the rule of the New York Produce Exchange requires, for an oil to be considered as a "pure natural oil," that it should exhibit a regular gradation in the densities of successive fractions.

When the Engler method is used for fractionating an oil, or when the amount of sample available is small, the ordinary rapid methods of determining the specific gravities of the fractions cannot be conveniently used. The author described an apparatus whereby the gravity of successive fractions may be determined rapidly during the distillation, the fractions being removed in succession or mixed, and the gradual change of density determined as the distillation proceeds. From the data obtained, curves may be plotted showing the behaviour of an oil during close fractionation, or the effect of cracking at any stage.

Some special difficulties found in the distillation of heavy asphaltic oils of Mexican origin were discussed, more especially in regard to the determination of water and the carrying of the distillation to the "coking stage."

A special distillation flask was described, whereby these difficulties are overcome by means of an electrically deposited copper coating to the flask, an electrically heated and controlled still-head, and the subsequent removal of adhering water in the side-neck and condenser tubes by means of absolute alcohol, which is then treated with magnesium amalgam and the evolved hydrogen measured.

169. "Mercuration of Aromatic Amines." (Preliminary Note). By GILBERT T. MORGAN and J. CAMPBELL ELLIOTT.

The circumstance that aromatic compounds containing metallic and metalloidal substituents are becoming in-

creasingly important in therapeutics renders the conditions of formation of these products a matter of considerable interest. The introduction into aromatic nuclei of arsenic, antimony, and similar metalloids involves reactions needing special precautions, and proceeding only slowly to completion. On the contrary, the mercuration of aromatic amines proceeds so rapidly and quantitatively that the process can be readily demonstrated as a lecture experiment. One grm. of aniline is added to 6.6 grms. of mercuric acetate dissolved in 300 cc. of cold methyl alcohol, and the solution boiled for two minutes. Another 6.6 grms. of mercuric acetate dissolved in 300 cc. of methyl alcohol are boiled for the same time, and serve for a control experiment. The two hot solutions are each poured into 300 cc. of water containing 7.5 grms. of potassium iodide. The control solution of mercuric acetate gives immediately yellow mercuric iodide, changing almost instantaneously into the stable red modification. The solution to which the aniline has been added no longer contains mercuric ions, the whole of the mercury having become attached to the aromatic nucleus. It yields a yellowish white precipitate of di- and tri-iodomercurianilines, which is quite distinct from the red precipitate obtained in the control experiment. *m*-Toluidine (1.1 grm.) may be substituted for aniline in the foregoing experiment, with a similar result, the yellowish white precipitate containing a mixture of di- and tri-iodomercuri *m*-toluidines (compare Schrauth and Schoeller, *Ber.*, 1912, xlv., 2808).

Other bases containing unsubstituted ortho- and para-positions behave in a similar manner. With methyl-aniline and dimethylaniline, similar proportions (2—3 molecules) of mercuric acetate are taken up, but the resulting yellowish white organic mercuri-iodides are discoloured by red and green oxidation products respectively. An analogous reaction occurs with diethylaniline, the amount of coloured by-product being less. Diphenylamine reacts with 5.6 molecular proportions of mercuric acetate, and yields a voluminous white organo-mercuri-iodide. Aromatic bases, partly substituted in their reactive ortho- and para-positions, are also readily mercurated, but the amount of mercuric acetate taken up diminishes as substitution increases. *o*-Toluidine and dimethyl-*o*-toluidine condense with two molecular proportions of mercuric acetate, and give white organo-mercuric iodides, but with the latter base the reaction proceeds very slowly. *p*-Toluidine reacts readily with 1 molecular proportion of mercuric acetate. Further treatment with more acetate leads to oxidation. Methyl *p*-toluidine and dimethyl-*p*-toluidine behave similarly.

α -Naphthylamine and β -naphthylamine condense, respectively, with one and two molecular proportions of mercuric acetate, and yield the corresponding organo-mercuric iodides (compare Brieger and Schulemann, *Journ. Pr. Chem.*, 1914, [2], lxxxix., 97).

When the foregoing organo-mercuric iodides are left in contact with hydriodic acid, some of the organically combined mercury is removed in the form of mercuric iodide, but these compounds are not affected by neutral iodides.

170. "The Viscosities of Mixtures of Formamide with the Alcohols." By SOLOMON ENGLISH and WILLIAM ERNEST STEPHEN TURNER.

In confirmation and extension of previous work (Merry and Turner, *Trans.*, 1914, cv., 748), the viscosities of mixtures of formamide with *n*-propyl, *isobutyl*, and *isoamyl* alcohols at 25° have been measured. It had previously been shown that with water, methyl alcohol, and ethyl alcohol, the negative deviation of the observed from the calculated viscosity grew less in the order of the substances named, and it was now shown that the deviation becomes positive with *n*-propyl alcohol, although the viscosity curve does not attain a maximum, and that the *isobutyl* and *isoamyl* alcohol curves each contains a maximum point. The *n*-propyl alcohol curve is sinuous, and the sinuosity is developed in the two higher alcohols, so that they contain,

not only a pronounced maximum, but also a minimum, point.

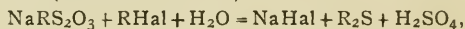
171. "Action of Nitro-substituted Aryl Haloids on Alkali Thiosulphates and Selenosulphates." By DOUGLAS FRANK TWISS.

Various investigations have already shown that the alkyl haloids can react with the alkali thiosulphates, giving the corresponding alkali alkyl thiosulphates; but the few corresponding aryl thiosulphates discovered hitherto have been prepared by less simple processes, usually depending on oxidation of a mixture of sodium thiosulphate and an aromatic substance.

Unsubstituted aryl haloids fail to react with sodium thiosulphate, but the 2:4-dinitro- and 2:4:6-trinitro-phenyl haloids readily enter into action with not more than a semimolecular proportion of sodium thiosulphate, yielding, not the corresponding organic thiosulphate compounds, which appear to be capable of only transient existence, but the corresponding sulphides. In a similar manner, reaction with not more than a semimolecular proportion of potassium selenosulphate produces the corresponding selenides.

When an excess of sodium thiosulphate is used with 4-chloro- or 4-bromo-1:3-dinitrobenzene, the resulting 2:4-dinitrophenyl sulphide is not the only product, for the solution subsequently deposits 2:4-dinitrophenyl disulphide. An excess of potassium selenosulphate yields almost exclusively 2:4-dinitrophenyl diselenide.

These results are explained by the primary formation of an unstable alkali aryl thiosulphate or selenosulphate which, in the presence of excess of aryl haloid, passes into the corresponding sulphide or selenide, according to the equation (for the former case)—



whilst with an excess of inorganic thiosulphate or selenosulphate the alkali aryl thiosulphate or selenosulphate produced subsequently decomposes, as their aliphatic analogues readily do, yielding disulphide or diselenide.

PHYSICAL SOCIETY.

Ordinary Meeting, June 12, 1914.

Prof. T. MATHER, F.R.S., Vice-President, in the Chair.

A PAPER entitled "Note on the Connection between the Method of Least Squares and the Fourier Method of Calculating the Coefficients of a Trigonometrical Series to Represent a given Function or Series of Observations," by Prof. C. H. LEES, F.R.S., was taken as read in the absence of the author.

In view of the number of alternative methods which have been suggested for calculating the coefficients of the terms of a Fourier series to represent a number of observations of a variable quantity, the author points out that the Fourier method gives the most probable values of the coefficients, since it makes the sum of the squares of the errors at the points of observation a minimum.

DISCUSSION.

DR. C. CHREE mentioned that the method was dealt with in Tait's "Natural Philosophy," but no proof was given. Prof. Lees had supplied the proof, and the paper was of interest on that account.

DR. W. WILSON (communicated remarks) said Prof. Lees deals with a function $f(x)$ of period l , whose values are given in the whole interval from 0 to l . In this case the validity and uniqueness of the Fourier expansion (provided $f(x)$ is subject to certain restrictions) have been demonstrated with complete rigour (Dirichlet, "Collected Works," vol. i., pp. 133—160, and G. Cantor, *Journal für Mathematik*, lxxii.). It seems to me therefore that there is no question of the reliability of the Fourier coefficients, and the fact that the method of least squares leads to the usual Fourier expressions for the coefficients confirms the

reliability of this method rather than that of the Fourier coefficients themselves.

A paper entitled "A Magnetograph for Measuring Variations in the Horizontal Intensity of the Earth's Magnetic Field" was read by Mr. F. E. SMITH.

In the case of unifilar instruments for recording variations in H , if θ is the angle which the magnetic system makes with the magnetic meridian, M the moment of the magnet, and H the horizontal intensity of the earth's field, equilibrium results when $MH \sin \theta = T\phi$, where ϕ is the torsion on the fibre and T is a constant. In the instrument described ϕ may be made great or small, but high sensitiveness is secured by making ϕ great. The magnet system is supported by a quartz fibre, and critically aperiodic damping is obtained by means of an aluminium vane and two parallel damping plates. To diminish the sensitiveness the effective length of the fibre may be reduced. The general usefulness of the instrument is illustrated by photographic records, which show the instrumental peculiarities to be very small, and indicate that unless the system is aperiodic increased difficulty must result in the interpretation of the records. An over-damped system responds but slightly to rapid pulsations in H , but follows the slow changes which are common all over the world. The general sensitiveness of the records is about 3 mm. for a change in H of 0.00001 C.G.S. unit, but one record shows a displacement of 8 mm. for such a change.

DISCUSSION.

DR. CHREE thought the instrument ingenious and likely to be very useful for the purpose for which he understood it was primarily intended, viz., the observation of the disturbances produced at the National Physical Laboratory by existing and prospective electrical tramways and railways. There were various features in the existing disturbances whose investigation seemed likely to be of interest and to the public advantage. There were also certain natural phenomena, for example, "pulsations," or small oscillations of magnetic force, for whose investigation the instrument from its great sensitiveness seemed well adapted, only for such purposes it would have to be set up at some station, such as Eskdalemuir, remote from London or any other large centre of electrical industry. There were, however, two features, viz., the somewhat rapid variation of scale value across the sheet, and the fact that the instrument responded sensibly to changes of declination as well as horizontal force, which, he thought, stood somewhat in the way of its employment for ordinary observatory purposes.

MR. R. S. WHIPPLE asked whether the author had considered the advisability of flashing a spot of light across the sheet to give the time scale, as was done at Potsdam.

MR. C. W. S. CRAWLEY considered the tramways were a great nuisance to magnetic observers. He had gone a good deal further in sensitiveness than the author, and even when situated 16 miles from the nearest tramways he had found them very troublesome. The little kick in the middle of the disturbance which Mr. Smith thought might be an instrumental error had often been noticed by him, and was a definite phenomenon in no way due to the instrument.

Prof. T. MATHER asked if the author had tried using the finest quartz fibre which he could handle. It appeared that the instrument took two or three seconds to attain its final position. If a finer fibre were used, a lighter and quicker magnetic system could be employed.

The AUTHOR, in reply, agreed with the remarks of Dr. Chree. He had thought it would be interesting to set up an instrument to detect very small pulsations, such as might occur during solar eclipses, while neglecting the larger ordinary disturbances. He admitted that the variation of sensitiveness across the sheet would be a disadvantage to an ordinary observatory assistant, but it gave him no trouble whatever. In reply to Mr. Whipple, he had already started to employ the flash of light method for the time

scale. In reply to Prof. Mather, there was no doubt that that the system could be made a good deal lighter if it were desired to measure very sudden disturbances lasting only a few seconds.

A paper entitled "*The Atomic Weight of Copper by Electrolysis*" was read by Mr. ALBERT G. SHRIMPTON.

Four copper cells separating two silver cells were run in series. The areas of the four copper cathodes increased from 10 to 50 s.c.s. By plotting the weights of the copper deposits against the corresponding areas of the cathodes, and extrapolating to zero area, the weight of the deposit is corrected for under experimental conditions. The atomic weight of copper = $\frac{\text{corrected weight of Cu}}{\text{mean weight of Ag}} \times 197.88 \times 2$.

The mean atomic weight for ten determinations = 65.563, with a mean error of ± 0.003 . To obtain a uniform coherent deposit of pure metal the following points were considered:—

1. Cylindrical cells with stationary and rotating cathodes were used.

The cathode current density must be kept below a certain limiting value to prevent the formation of non-coherent deposits, due to secondary deposition. This was found to depend upon the geometry of the cell, the concentration of the electrolyte, the presence of acids and other impurities, the addition of a porous pot, and the rate of revolution of the cathode. Formulæ are given by which the limiting cathode current density can be found for all conditions of the cell for Cu, Ag, Au, and Zn.

3. To prevent the formation of loose crystalline clusters the current density must also be kept below a certain value depending upon the weight to be deposited. (Formulæ are given).

DISCUSSION.

Mr. F. E. SMITH congratulated the author on the results of his work. He appeared to have triumphed over many difficulties, and for his particular purpose had converted the copper voltameter from an instrument of error into an instrument of precision. In future work he hoped that Mr. Shrimpton would avoid the use of common porous pots. They might produce trouble, and were not necessary, as all voltameter work could now be carried out without the introduction of any medium between anode and cathode. He should be pleased to give Mr. Shrimpton full particulars. The statement respecting deposition of hydrogen was, he thought, incorrect. It was not logical to assume that hydrogen ions were first deposited because of the lack of copper in the neighbourhood of the cathode, and then to state that as soon as they were deposited they went into solution again, and in doing so displaced copper from the solution. With regard to crystalline growths at the bottom of the cathode, he believed these were due to the high current density at the base due to the passage of the current through the liquid descending from the anode. There was also a possibility that the electrolyte was not quite pure. In the silver voltameter he had obtained striated deposits with impure electrolytes, but not with pure solutions. Mr. Shrimpton also stated that silver deposits from acidified solutions were normal; this was not his experience, nor that of other investigators. He believed the deposit to be less in mass when the electrolyte was acid. A rather important question arose with regard to any Cu_2SO_4 which might be formed in the cathode space. Richards (who also extrapolated to zero area, as Mr. Shrimpton had done) remarked in his paper: "A value obtained in this way must correspond to a deposit of copper slightly too great; for the mode of correction (*i.e.*, extrapolation to zero area) does not take account of the growing, although slight, presence of cuprous salts." Mr. Shrimpton said the extrapolation to zero area covered this case. The speaker thought the point was one that should be settled. Of course, when one reduced the area the current density at the cathode was increased, and so also was the fall of potential near the cathode; this might have some influence.

Dr. J. H. VINCENT mentioned that after working out the conditions necessary for satisfactory results, the author had performed the ten determinations quoted in the paper straight away, no results being rejected. As they all came within 1 part in 6000 of the mean there appeared to be no doubt that the correct conditions for satisfactory working had been obtained.

Dr. S. W. J. SMITH thought the author's views on secondary deposition could not be correct as they stood, although it was conceivable that sudden variations in the surface concentration of the copper sulphate, due to irregularities of convection, might make it possible for hydrogen to be deposited at one moment and to go into solution again at the next. Non-coherent deposits could be explained without invoking the aid of hydrogen. He thought the author's empirical conclusion, that the limiting current density depends upon the concentration of non-ionised molecules, had some theoretical support.

A paper entitled "*Note on an Improvement in the Einthoven String Galvanometer*," by Mr. W. H. APHORPE, was taken as read.

The instrument was exhibited at Cambridge on June 20.

NOTICES OF BOOKS.

A Manual of Practical Physical Chemistry. By FRANCIS W. GRAY, M.A., D.Sc. London: Macmillan and Co., Ltd. 1914.

This book contains a collection of exercises in physical chemistry, each of which can be performed by the student in a period of from two to three hours. Usually speaking the apparatus would have to be put together beforehand, and a few extra experiments are added which would require considerably more time for performance. Thermochemistry, polarimetry, and electrochemistry are included, and very clear diagrams of apparatus are given, while the directions are usually full and precise. In some cases help from a demonstrator might be required, but generally speaking the well-prepared student should be able to carry out the experiments quite unaided and calculate the results. The theoretical principles of the methods are shortly explained, and a very useful introduction on accuracy deals carefully with the calculation of average errors and similar questions.

Notes on Elementary Inorganic Chemistry. By F. H. JEFFERY, M.A. Cambridge: The University Press. 1914.

A CURSORY examination of this book suggests that it consists of a collection of disjointed facts and that it exhibits but little cohesion. But if the text is read more carefully it will be found that the author has very skilfully selected for notice the details which the beginner finds most puzzling or most difficult to retain in his memory. Occasionally it would appear that unnecessary matter has been included, such as the lists of salts, oxides, &c., but on the other hand some of the chapters, as for example those on oxidation and reduction, the identification of some common gases, and the action of heat upon salts and of acids on metals, are well planned. For revision purposes the book will be very useful, and although the ideal plan would be for the student to prepare such a summary for himself, basing it upon his lecture and laboratory work, if this is out of the question for lack of time the use of the book will certainly help to fix and establish his knowledge.

The Curious Lore of Precious Stones. By GEORGE FREDERICK KUNZ, A.M., Ph.D., D.Sc. Philadelphia and London: J. B. Lippincott Company. 1913.

The author of this book has a unique knowledge of the uses of precious stones in religion, medicine, &c., and has moreover acquired what is believed to be the most com-

prehensive private library on the subject in existence. Hence he is particularly well qualified to produce a book which treats exhaustively of the use of precious stones at different periods by the peoples of all nations, and describes the many superstitions connected with them. The book is beautifully illustrated by coloured plates and double tones, and is full of curious anecdotes from old documents. The chapters on ominous and luminous stones and on crystals and crystal gazing are particularly interesting.

How to Build up Furnace Efficiency. By JOS. W. HAYS. Seventh Edition. Chicago: Jos. W. Hays. 1914.

THIS pamphlet contains a spirited discussion in highly colloquial language of the question of fuel economy and furnace efficiency, and is sure to make a considerable impression upon the practical man into whose hands it happens to fall. The author has had much experience in detecting defects in furnaces, and he has certainly profited by it. He has no false pride about confessing his mistakes, and he does not hesitate to take his readers into his confidence about "occasions on which he has made a fool of himself," and even provides an illustration to drive the lesson home. The book is written for the unlettered man who would be quite unequal to the task of tackling a treatise on fuel economy, and many anecdotes are given to illustrate the author's conclusions and to awaken the reader's interest.

Electric Switches for Use in Gaseous Mines. By H. H. CLARK and R. W. CROCKER. Washington: Government Printing Office. 1913.

THIS bulletin describes an interesting series of tests carried out with switches of both the explosion proof and oil types. The experiments were of a preliminary nature only, and were performed principally for the purpose of obtaining information upon which future tests could be based. Eight different types of switch are described in the bulletin, with criticisms of their designs and discussions of the results of the tests. Of the eight types only one was found to be really suitable for use in mines. The Bureau intends to carry out a further series of tests and to base upon them a list of switches suitable for use in gaseous mines.

Critical Ranges A₂ and A₃ of Pure Iron. By G. K. BURGESS and J. J. CROWE. Washington: Government Printing Office. 1914.

THIS bulletin contains a critical and historical summary of previous experimental observations of the location of the A₂ and A₃ points of pure iron, and also gives an account of a series of fresh experiments carried out by the authors. The thermal methods used were the inverse-rate method of Osmond and the derived differential method of Rosenhain, and special precautions were taken to ensure the accuracy of the results. The temperature ranged from 500–1000°, and the authors believe that they have established a definite transformation at 768°, and a less well-defined though more intense one at 898 to 909°.

The New International Metric Diamond Carat of 200 Milligrams. By GEORGE FREDERICK KUNZ.

THIS pamphlet contains a paper read before the American Institute of Mining Engineers at the New York meeting in 1913. It gives an account of the events which have led to the adoption of the metric carat, which is now legalised in most of the countries of Europe. There is no doubt that its adoption will be universal in the near future, and the advantages of using a single standard of weight in all countries, and one which moreover is decimally divided, are obvious. The pamphlet gives rules, with worked out examples, for calculating the weights and prices of diamonds under the new and old standards.

CHEMICAL NOTICES FROM FOREIGN SOURCES

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

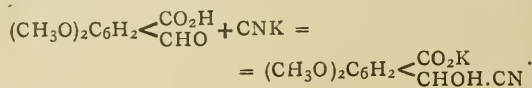
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 18, May 4, 1914.

Chloro-iridate and Chloro-iridite of Lithium.—Marcel Delépine.—The compositions of the chloro-iridate and chloro-iridite of lithium are the same as those of the corresponding salts of sodium. In a mixture of the chloro-salts of lithium and sodium the latter separate first, with very little lithium. If the crystallisation is continued mixed crystals are obtained which, from $\text{IrCl}_6\text{Na}_2\text{Li}$ to $\text{IrCl}_6\text{NaLi}_2$, have a very much elongated crystalline form differing from the rhombohedral form in which the single sodium or lithium salts crystallise.

Bulletin de la Société Chimique de France.
Vol. xv., No. 10, 1914.

Preparation of Glycide.—Jean Nivière.—Bigot prepared glycide by the action of sodium on monochlorohydrine, but the process was very slow. The author has improved the yield and hastened the process by the following modification:—340 grms. of monochlorohydrine are mixed with three times their volume of absolute ether. The mixture is placed in a flask furnished with an ascending condenser and immersed in a water-bath. 65 grms. of sodium are gradually added in small portions of about 2 grms. The temperature is not allowed to exceed 40°. When all the sodium has disappeared the ethereal solution is decanted off, and the sodium chloride is washed with absolute ether and then with a mixture of ether and anhydrous alcohol. The ethereal solutions are distilled, and when the solvent is eliminated the residue in the flask is rectified *in vacuo*. Between 60° and 100° under 15 mm. glycide passes over.

Meconine Carboxylic Acid.—P. Freundler.—Meconine carboxylic acid is easily obtained by condensing opianic acid with potassium cyanide. At first a brown solution is obtained, which contains the potassium salt of the free oxy acid:—



When hydrochloric acid is added a brown viscous oil is deposited. This is probably the raw lactonic nitrile, and on saponification on the water-bath meconine carboxylic acid is formed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvii., No. 7, 1914.

Syntheses of New Glucosides.—Emil Fischer.—The author, in collaboration with Helferich, has recently shown that the silver salts of the purines react with aceto-bromo-glucose in anhydrous solvents, and a simple synthesis of purin glucosides can be based upon this reaction. The author has now further shown that many other sugar derivatives can be prepared similarly. Thus aceto-bromo-glucose and dry silver succinimide react in xylol solution at the temperature of the water-bath, giving a good yield of tetra-acetyl-succinimide-glucoside. The acetyl groups can be removed by treatment with methyl alcohol ammonia, but at the same time a product, $\text{C}_4\text{H}_7\text{O}_2 \cdot \text{C}_6\text{H}_{11}\text{O}_5$, which appears to be the glucoside of succinamide, is formed.

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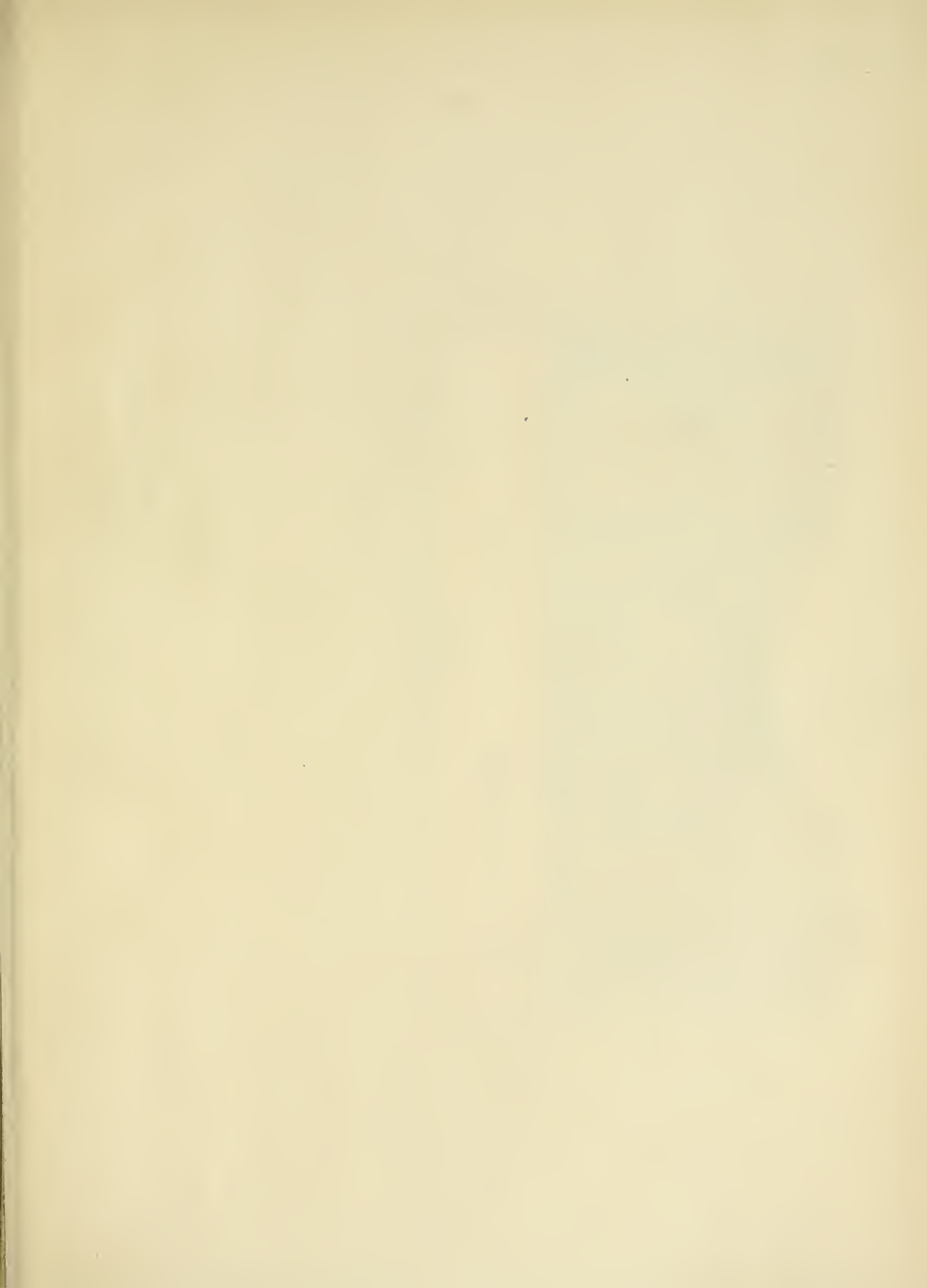
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